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SULPHUR ISOTOPES IN THE WHITE PINE MINE,
ONTONAGON COUNTY, MICHIGAN

by

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SCOPE AND CONTENTS: Ore specimens from the cupriferous zone of the basal Nonesuch shale at the White Pine Mine were analysed for sulphur isotopes, carbon and sulphide contents and boron. The results of the analyses were discussed in relation to a biogenic-syngenetic mineralization process for the ore body. A model, based on the $\delta S^{34}_{\text{sulphide}}$ frequency distribution, was developed to determine the $\delta S^{34}_{\text{sulphate}}$ value of the lower Nonesuch paleoenvironment. A transmitted light microscopic examination of chlorite was undertaken in order to present a more complete picture of this proposed source for copper in the cupriferous zone of the Nonesuch shale.

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ABSTRACT

The range and standard deviation (σ) of $\delta S^{34}_{\text{sulphide}}$ from 94 specimens of White Pine ore indicate a biogenic origin for the sulphide in this Precambrian deposit. Assuming that a common interval of biogenic fractionation effects ($\delta S^{34}_{\text{sulphate}} - \delta S^{34}_{\text{sulphide}}$) from 0 to 25 per mil applies to the Precambrian sulphate reducers, and assuming that this interval may be approximated by the 2σ of the $\delta S^{34}_{\text{sulphide}}$ frequency distribution for the cupriferous zone, then the $\delta S^{34}_{\text{sulphate}}$ value of the lower Nonesuch paleoenvironment can be estimated as $+15 \pm 2‰$. A comparison of mean $\delta S^{34}_{\text{sulphide}}$ values for the #23, #26, and #43 beds, and for the cupriferous zone adjacent to the transition zone indicates a trend to lighter $\delta S^{34}_{\text{sulphide}}$ values from the #23 bed upwards.

Contours of the areal distribution of $\delta S^{34}_{\text{sulphide}}$ values and of the weight per cent sulphide for the sediments in the #23 and #43 beds indicate definite trends. The trends in the #23 bed outline the sedimentological aspects of this unit. In the #43 bed, the contour trends reflect the sedimentology of the immediately underlying #30 unit (upper sandstone). The relationship between these trends and the sedimentology of the cupriferous zone strongly supports a biogenic origin for the sulphide. The significant negative correlation between $\delta S^{34}_{\text{sulphide}}$ and % S^{-2} for the #43 bed is clearly related to the areal distribution of these variables. A similar negative correlation between $\delta S^{34}_{\text{sulphide}}$ and % S^{-2} for the #23 bed, when adjusted for an epigenetic sulphide enrichment, is not so clearly related to the areal distribution of these parameters. It is possible that the negative correlations between $\delta S^{34}_{\text{sulphide}}$

and % S^{-2}, and the relationship of these parameters to their areal distribution, in the #43 bed, is a function of the metabolism and the areal distribution of the Precambrian sulphate reducers. Contoured areal sulphide distributions in combination with a plot of $\delta S^{34}_{\text{sulphide}}$ vs. % S^{-2} for the #23 unit define an epigenetic component of the sulphide mineralization that is related to the White Pine fault.

A positive correlation exists between weight per cent carbon and weight per cent sulphide in the #23 and #43 beds. However, no correlation exists between these variables in the #26 bed. This is unusual if the ore, as is the case for the #23 and #43 units, is related to the occurrence of organic matter. The positive correlation between % C and % S^{-2} implies a negative correlation between % C and $\delta S^{34}_{\text{sulphide}}$ within the #43 bed. This negative correlation differs from the positive correlation between these two variables determined empirically in the laboratory (Kemp and Thode, 1968). The difference between the field and laboratory relationships can be resolved by considering 1) the nutrient carbon/size of bacterial population ratio and 2) the diluting effect of the sediments.

Boron analyses of the cupriferous zone samples suggest a brackish to fresh water paleoenvironment for the basal Nonesuch shale. The similarity between the ranges in boron values within the cupriferous and pyrite zones does not support an epigenetic mineralization hypothesis for the White Pine ore body.

CHAPTER I

THE WHITE PINE MINE

Section 1: Introduction

The Precambrian White Pine copper deposit is located at the town of White Pine in Northern Michigan which is situated west of the base of the Keweenaw Peninsula approximately 14 miles S.W. of Ontonagon, Michigan (see Figure I-1). The ore body, mined by the White Pine Copper Company, a wholly owned subsidiary of the Copper Range Company, lies within a belt of copper mineralization that extends some 160 miles N.E. from Mellen, Wisconsin, to the tip of the Keweenaw Peninsula.

Copper was first mined in the White Pine area in 1865 from the Nonesuch Mine 2 miles east of White Pine. Here native copper and silver were mined from the sandstone beds at the base of the Nonesuch Shale.

Over a period from 1915 to 1921 copper was economically extracted from the old White Pine Mine. The ore was located in the sandstones at the base of the Nonesuch Shale along a native copper enriched zone adjacent to the White Pine fault. However, the extent of the ore was not great and the Mine stopped operations around 1921.

In 1937 the Copper Range Company acquired the White Pine property and undertook an exploratory drilling programme that in 1942 proved a copper shale ore deposit averaging about 1% copper. With the develop-

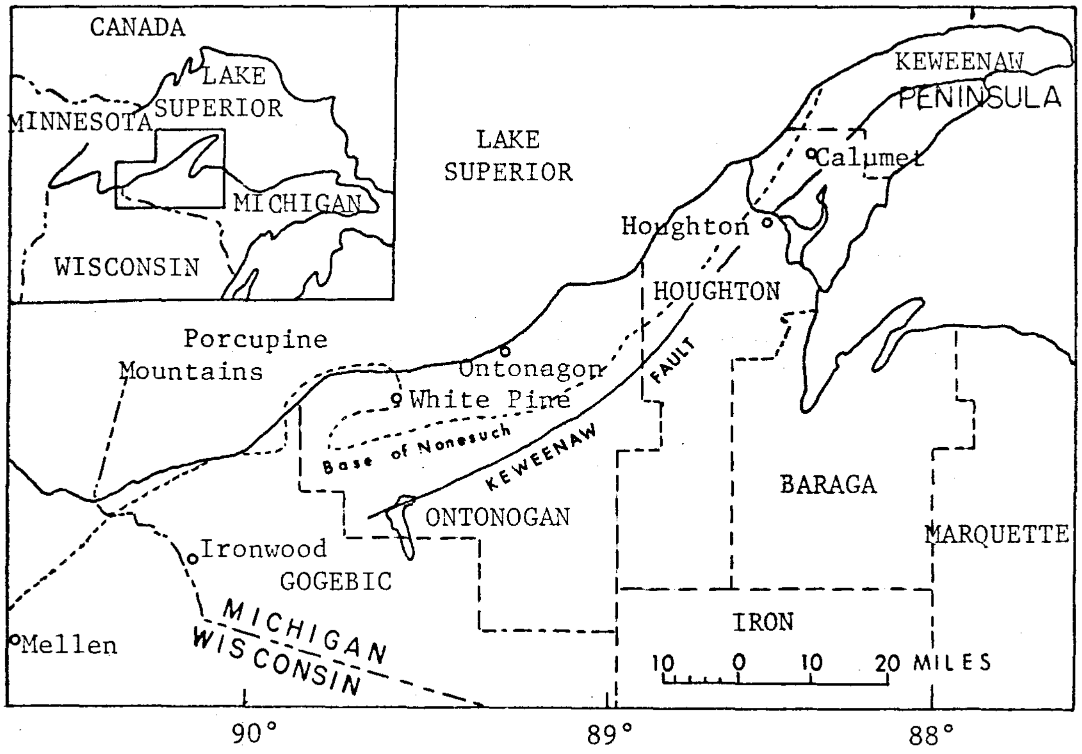

Figure I-1: Location of the White Pine District

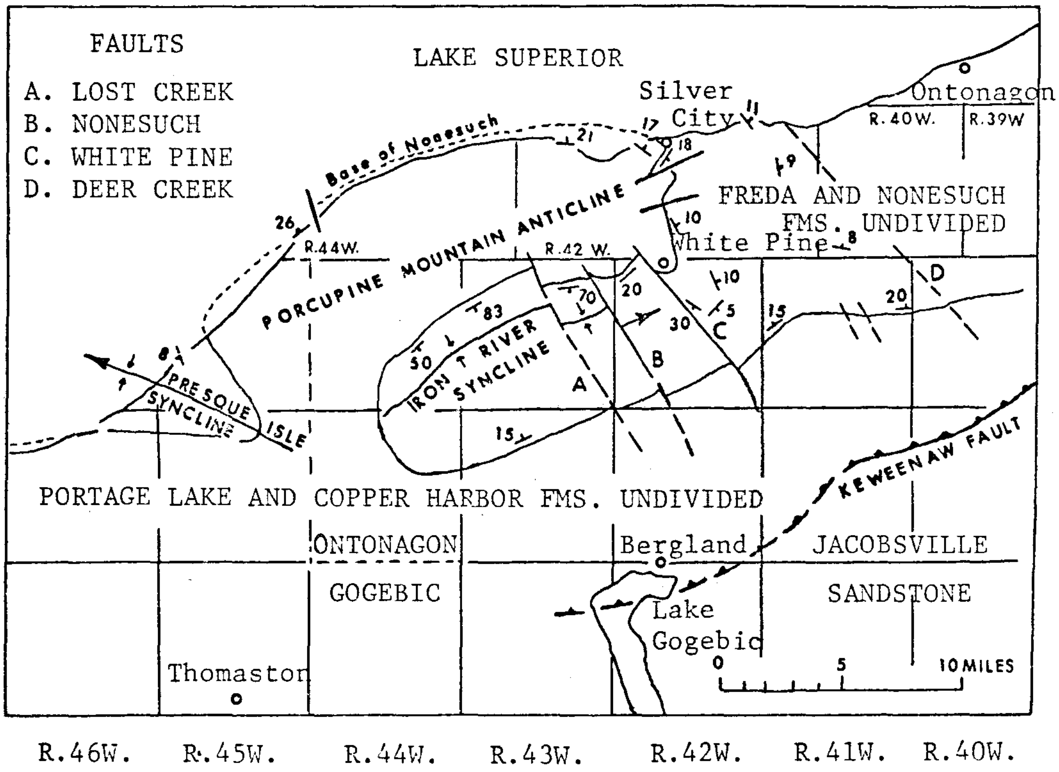

Figure I-4: Geologic Sketch Map of the White Pine-Porcupine Mountain District
(from Ridge, 1968)

ment of froth-flotation ore separation techniques the Schacht shaft was mined on an experimental basis in 1945. Further exploratory drilling and a successful milling research programme led, by 1953, to the full scale mining operation of the present White Pine Copper Company.

Since 1961, the average grade of ore mined has been slightly over 1.2%. The current mining rate of 17,000 tons per day ranks the White Pine Mine as one of the largest underground copper mines in North America. At this mining rate and considering the ore reserves that underlie some 20 square miles of land, the life of the ore deposit can be estimated as more than 100 years.

Section 2: Previous Studies

The White Pine copper sulphide deposit, its stratigraphy, geochemistry, extent and type of mineralization has been very adequately discussed by White and Wright (1954, 1966), Wiese (1960), Carpenter (1963), Brown (1965, 1968), Hamilton (1967) and Jost (1968). These later studies deal primarily with the problem of the copper mineralization of the lower Nonesuch Shale and uppermost Copper Harbor Conglomerate, in particular the transgressive nature of the upper and lower boundary of the cupriferous zone. Earlier studies of the copper mineralization of the Nonesuch Shale and the Copper Harbor Conglomerate have been made by Whittlesey (1877), Nishio (1919), and Butler and Burbank (1929).*

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* See White and Wright (1954) for a more complete bibliography on earlier studies of the copper mineralization of the Nonesuch shale.

Section 3: Stratigraphy (The following summary of the stratigraphy is largely taken from White and Wright, 1954)

The Nonesuch Shale consists of virtually unmetamorphosed dominantly grey, interbedded siltstones and shales of late Precambrian age. The formation is overlain by and transitional into the red to brown colored, coarser grained Freda sandstone, and overlies the much coarser grained Copper Harbor conglomerate (see Figure I-2). At Calumet, Michigan, and Mellen, Wisconsin, the Nonesuch shale is respectively 700 and 250 feet in thickness. Between these two towns the shale averages 600 feet in thickness. This formation dips at an angle of 15° to 45° N. to N.W. towards Lake Superior, and disappears to the west mostly as a result of a change in sedimentary facies.

At the White Pine Mine, copper mineralization is restricted to the cupriferous zone which consists of the lowermost 25 to 50 feet of the Nonesuch shale and the uppermost 1 to 20 feet, the chloritic facies (Hamilton, 1967), of the Copper Harbor conglomerate. Stratigraphically, the cupriferous zone consists of a repeated sequence of: sandstone; thinly interlaminated shale and siltstone; massive grey siltstone, reddish near the base; evenly laminated siltstone, with grey shale partings below and red above (see Figure I-3). It is the opinion of White and Wright (1954) that the shale and siltstone parts of the two sedimentary sequences were deposited over their basal sandstones during two transgressions. The first of the two transgressive groups of shales and siltstones is defined by the parting shale which immediately overlies the lower sandstone (uppermost Copper Harbor conglomerate) and is transitional from it through a very thin 3 inch to 6 inch siltstone bed. The parting shale consists of finely laminated red to dark grey siltstone and shale

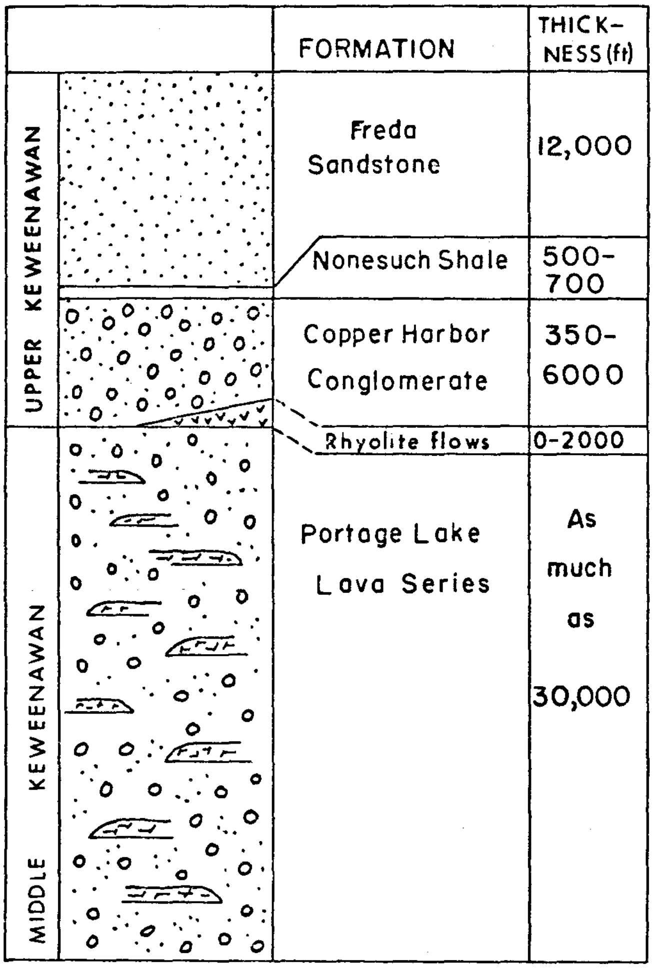

Figure I-2 Stratigraphic column of the Keweenaw Series in the White Pine District.

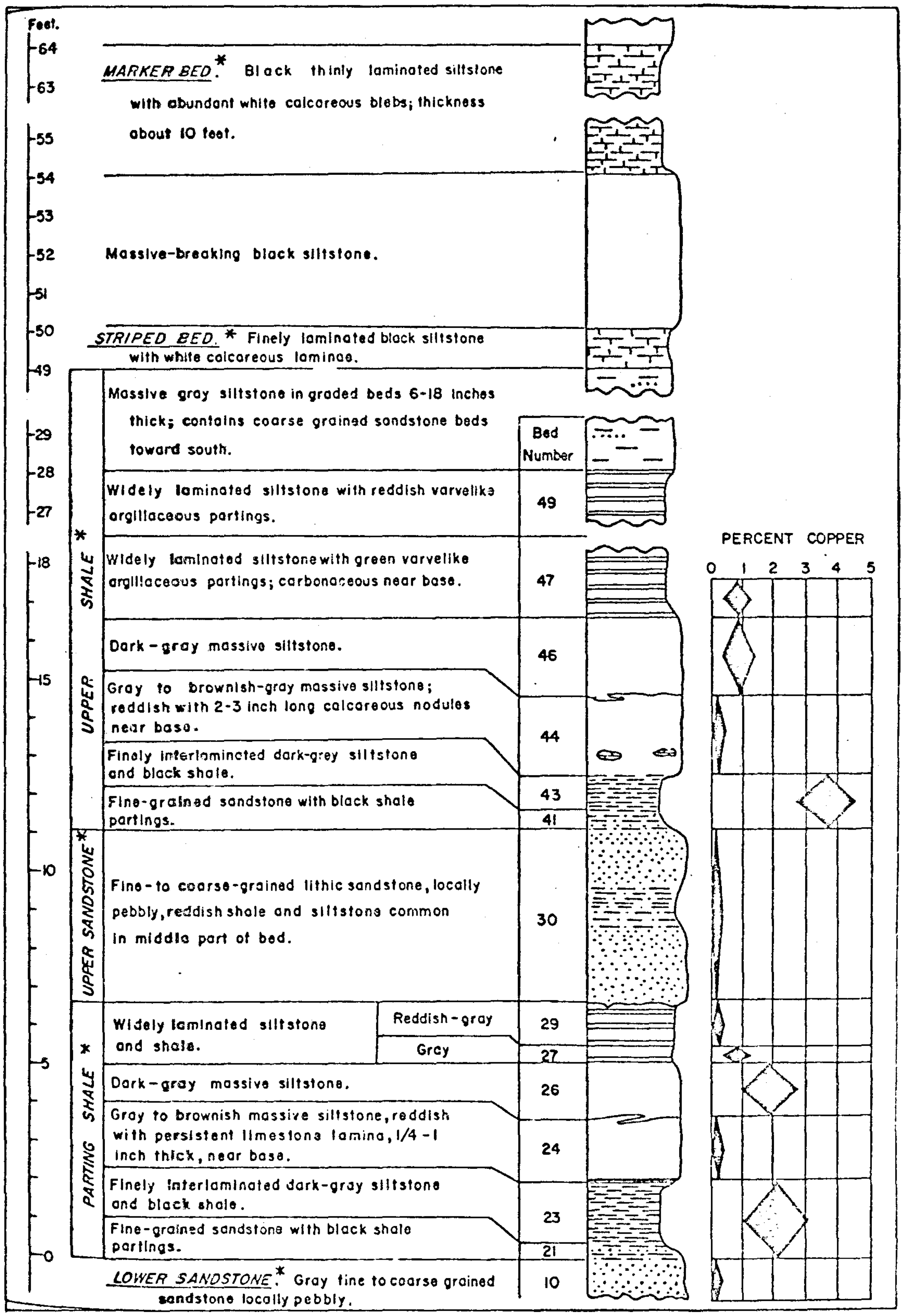

Figure I-3: Columnar section of the stratigraphy of the basal Nonesuch shale, at White Pine

* Denotes names of local usage

units. Individual laminae may be as thin as 10μ and pinch out over a few millimetres or inches, while the units vary on the average from one to four feet in thickness and are continuous over several square miles. The parting shale and overlying upper shale are recognizeable in the White Pine and Presque Isle regions indicating an extent over many tens of square miles (see White and Wright, 1966). Mudcracks are common at the top of the parting shale (#29 bed) and indicate a shallowing of the sedimentary basin before the deposition of the immediately overlying upper sandstone.

The upper sandstone, the basal sandstone of the second sedimentary sequence, frequently cuts into the underlying shale unit forming N.E. trending channels which are traceable within the Mine. This sandstone is finer grained than its counterpart in the first sedimentary sequence, the lower sandstone, and is more variable in both thickness and lithology. Its thickness averages 4 1/2 feet and its lithology varies from a massive, even grained sandstone to a sequence of graded sandstones interbedded with siltstones and red shales.

The next 7 to 8 feet of laminated siltstones and shales comprise 5 units of the second transgressive interval, the upper shale, that contain economic copper mineralization and have counterparts in the parting shale below. In total the upper shale consists of 20 to 40 feet of sediments. Its lowermost bed, #43, like the #23 bed of the parting shale, is transitional to the immediately underlying basal sandstone through a thin siltstone bed (see Figure I-3).

Very small amounts of copper mineralization occur throughout the cupriferous zone. However, considerable concentrations of copper as chalcocite and the native metal, locally over 10 weight percent, occur in the #23 and #26 units of the parting shale and the #43 and #46 units of the upper shale (see Figure I-3).

Section 4: Structure

Generally in Northern Michigan, the Nonesuch shale dips gently north and northwest towards the centre of the Lake Superior basin. However, in the area of the detailed map (see Figure I-1) the Nonesuch sediments have been downfolded into the Presque Isle and Iron River synclines which are located respectively to the S.W. and N.E. of the Porcupine Mountains. At the southern edge of the Porcupine dome the sediments have been overturned while along the northern flanks of this dome they have only been faulted.

The White Pine Mine is situated along the N.E. - S.W. trending axis of the Iron River syncline (see Figure I-4). The dominant structural feature in this area is the White Pine fault. This right handed tear fault strikes N.W. and dips steeply to the N.E. Its horizontal displacement has been estimated in the S.W. end of the mine as 2500 to 5000 feet. The vertical displacement of the fault is variable from only 240 feet in the S.E. end to about 1500 feet in the S.W. end of the Mine. Numerous minor, dominantly strike slip faults with a small vertical component and variable dip and strike are common in the White Pine Mine. They are related in frequency to the major White Pine fault. Earlier fractures related to the compaction of the Nonesuch sediments during lithification are also common. A fold formed by drag along the White Pine fault disturbs the sediments for some 10,000 feet to the N.E. of the fault at the White Pine Mine. The anticline increases in curvature as the fault is approached and the trend of its axial plane appears to roughly parallel the azimuth of the fault plane

Section 5: Silicate Mineralogy of the Sandstones and Siltstones-Shales

Both the upper and lower sandstones are immature lithic arenites containing abundant fragments of acid and basic volcanics. According to Jost (1968) quartz is the major component of the rock. Acid and basic magmatites comprise 20% to 30% of the rock, and feldspar (dominantly K-feldspar) makes up 3% to 8% of the sandstone. Clastic opaque iron oxide grains are common in most of the Copper Harbor conglomerate, but rare in the cupriferous lower and upper sandstones. In these, chlorite is the dominant cement occurring as radial blades rimming the sandstone grains, and imparting an overall greenish colour to the rock. Calcite and quartz are also common cements and locally carbonaceous matter with or without native copper may be an abundant cement.

Generally the siltstones consist of small, 20 to 40μ, grains of quartz, feldspar (dominantly albitic plagioclase) and subordinate volcanic rock fragments. These are set in an abundant matrix consisting of dominantly chlorite with sericite. Silica is not an uncommon cement in the coarser siltstone fractions, and carbonate cement is rare in the cupriferous siltstones. X-ray modal analyses have been done by Wiese (1960) and Moore _et al_ (1969) and wet chemical analyses have been done by Dr. Takuya Imai* and Moore _et al_ (1969). A few of these analyses are presented in Table I-1.

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* Analyst at Toshiba Denko Laboratory, Tokyo, Japan

TABLE I-1: Wet Chemical and Modal Analyses of the Nonesuch Shale

A) Modal Analyses

	Wiese (1960)				Moore *et al* (1969)
	Bed #23	Bed #23	Bed #26	Bed #26	Bed #23
Quartz	20	26	27	29	25
Chlorite	34	33	28	34	35
Muscovite	10	9	10	12	
Illitic mineral					25
Albite	15	17	14	17	10
Orthoclase	4.0	5.0	4.5	4.5	
Hematite	1.0	0.5	0.5	0.5	
Epidote	4.0	3.0	2.0	3.0	
Chalcocite	4.5	6.0	2.5	3.5	
TOTAL	92.5	98.5	88.5	103.5	95.0

TABLE I-1: Continued

B) Wet Chemical Analyses

	Takuya Imai*				Moore et al (1969)
	Bed #23	Bed #23	Bed #26	Bed #26	Bed #23
SiO_2	51.97	51.99	58.30	58.11	49.83
Al_2O_3	14.94	14.79	14.92	15.44	15.30
Fe_2O_3	1.10	-	1.76	2.12	1.26
FeO	5.99	6.80	6.53	5.92	4.97
MgO	3.61	3.68	4.75	4.69	3.72
CaO	1.20	1.02	0.12	0.08	1.32
Na_2O	1.78	1.99	2.07	1.99	1.91
K_2O	2.79	2.60	2.24	2.20	2.66
H_2O^+	2.39	2.74	3.12	2.83	3.92
H_2O^-	1.06	1.01	0.68	0.68	0.43
TiO_2	1.26	1.52	1.22	1.30	1.44
P_2O_5	0.24	0.25	0.20	0.20	0.22
MnO	0.10	0.09	0.09	0.11	0.17
CO_2	-	-	-	0.07	0.13
Fr. C	0.46	0.34	0.25	0.26	0.66
S	1.78	1.70	0.46	0.49	1.22
Cu	8.74	9.18	2.78	2.78	10.44
	99.41	99.70	99.49	99.27	99.27

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* Analyst at Toshiba Denko Laboratory, Tokyo, Japan

The uniformity in mineralogy and major element content is evident in the information presented in this table. Little information is available on the variation of trace elements within the cupriferous zone. Moore et al (1969) have completed two trace element analyses of one sample, presumably from the #23 bed. Their results indicate that the Nonesuch Shale is too poor in Pb, Zn, and V and too rich in Cu and Ti to be comparable to the Permian Kupferschiefer deposit in Germany. On the basis of trace element content, with the exception of Cu, the White Pine deposit compares best with the Scottish Oil Shale.

Section 6: The Metamorphic Grade, and the Age of the Lower Nonesuch Shale at the White Pine Mine

Due to the presence of low temperature orthorhombic chalcocite and thermally unstable carbon compounds such as vanadyl porphyrins (Barghoorn et al, 1965) it is doubtful that the Nonesuch shale at the White Pine Mine has experienced anything but a very mild metamorphic history with temperatures probably no greater than 100°C as suggested by Brown (1968).

Section 7: Ore Mineralogy

(a) Ore Minerals

The dominant metallic minerals in the White Pine deposit are exclusively copper varieties, namely: chalcocite (Cu_2S), native copper, Bornite (Cu_5FeS_4), covellite (CuS), chalcopyrite ($CuFeS_2$), digenite (Cu_9S_5), cuprite (Cu_2O), and a few other unidentified copper minerals (Jost, 1968; Brown, 1968). Grain counts of parting shale ore concentrates from the Schacht shaft determined that 87% of the mineralization was in the form of chalcocite and 13% was native copper. Bornite, covellite and calcopyrite were identified in the concentrates, but only in very small quantities, respectively, 14ppm, 10ppm and 5ppm. Native silver is a volumetrically unimportant mineral, present only in trace amounts, but of great economic value. Jost (1968) determined the modal abundance of ore minerals within three profiles at the White Pine Mine. His results are presented in Table I-2. The average abundance of copper in the four principally mineralized units of the cupriferous zone is illustrated in Figure I-3. However, not included in this diagram is the copper grade of the upper and lower sandstones adjacent to the White Pine fault. Here both these units contain sporadic but economic amounts of interstitial copper mineralization dominantly as native copper. These sandstone beds were mined at the turn of the century in the old White Pine Mine (see Figure IV-9a). The upper and lower sandstones do not contain economic quantities of copper throughout the remaining and by far greatest part of the White Pine Mine.

In the cupriferous zone at the White Pine Mine, most of the copper mineralization is controlled in occurrence and abundance by the sedimentological aspects of its host rock. Chalcocite* occurs as fine interstitial disseminated grains which are commonly 5 to 30 μ in diameter, and as lenses, seams and nodules up to a few millimetres across within the chloritic, carbonaceous, finer grained, laminated siltstones

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* Refer to White and Wright (1966) and Jost (1968) for a more thorough description.

TABLE I-2:* Modal % of Ore Minerals, from Jost (1968)

Bed #	Native Copper		**Copper Sulphides		Bornite		Chalcopyrite		Pyrite	
	1	2	1	2	1	2	1	2	1	2
#47 Bed	-	-	+	-	-	-	-	+	+	+
#46 Bed	0.2%	-	0.5%	0.4%	-	+	-	+	-	-
#43 Bed	0.7%	-	0.5%	6.2	-	-	-	-	-	-
	3		3		3		3		3	
#27 Bed	-	-	+	+	-	+	-	+	+	+
#26 Bed	0.4%	-	2.7%	0.5%	-	-	-	-	-	-
#23 Bed	0.6%	0.6%	3.0%	3.7%	-	-	-	-	-	-

1: Profile 30cc; 2: Profile N62; 3: Profile 33 3/8F

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* The significance of the + and - signs in this table were not defined by Jost (1968) in the translated version of his thesis. Presumably the + sign indicates that the mineral was present in a very small amount, while the - sign indicates that the mineral was absent from the sample examined.

** "Copper Sulphides" generally consists of 90% chalcocite and 10% digenite.

and shales. Commonly chalcocite occurs as 3 to 10 μ inclusions within the abundant chlorite in the interlaminated siltstones and shales (see Chapter IV section 5 of this thesis). Bedding, and the content of chlorite and carbon appear to exert the strongest control on the occurrence of chalcocite in the lower Nonesuch shale.

The green chloritic lower sandstone contains interstitial chalcocite largely as nodules, up to 5mm across, and as fine disseminations (see Hamilton, 1967). The chalcocite content in the uppermost Copper Harbor conglomerate is less than 0.5% by volume, much less than the maximum amount of native copper, 6 volume % (Hamilton, 1967). It is interesting that chalcocite inclusions have not been reported within the abundant "diagenetic" chlorites in the lower and upper sandstones. This must indicate some fundamental difference between these chlorites and the chalcocite bearing chlorites in the copper mineralized siltstones.

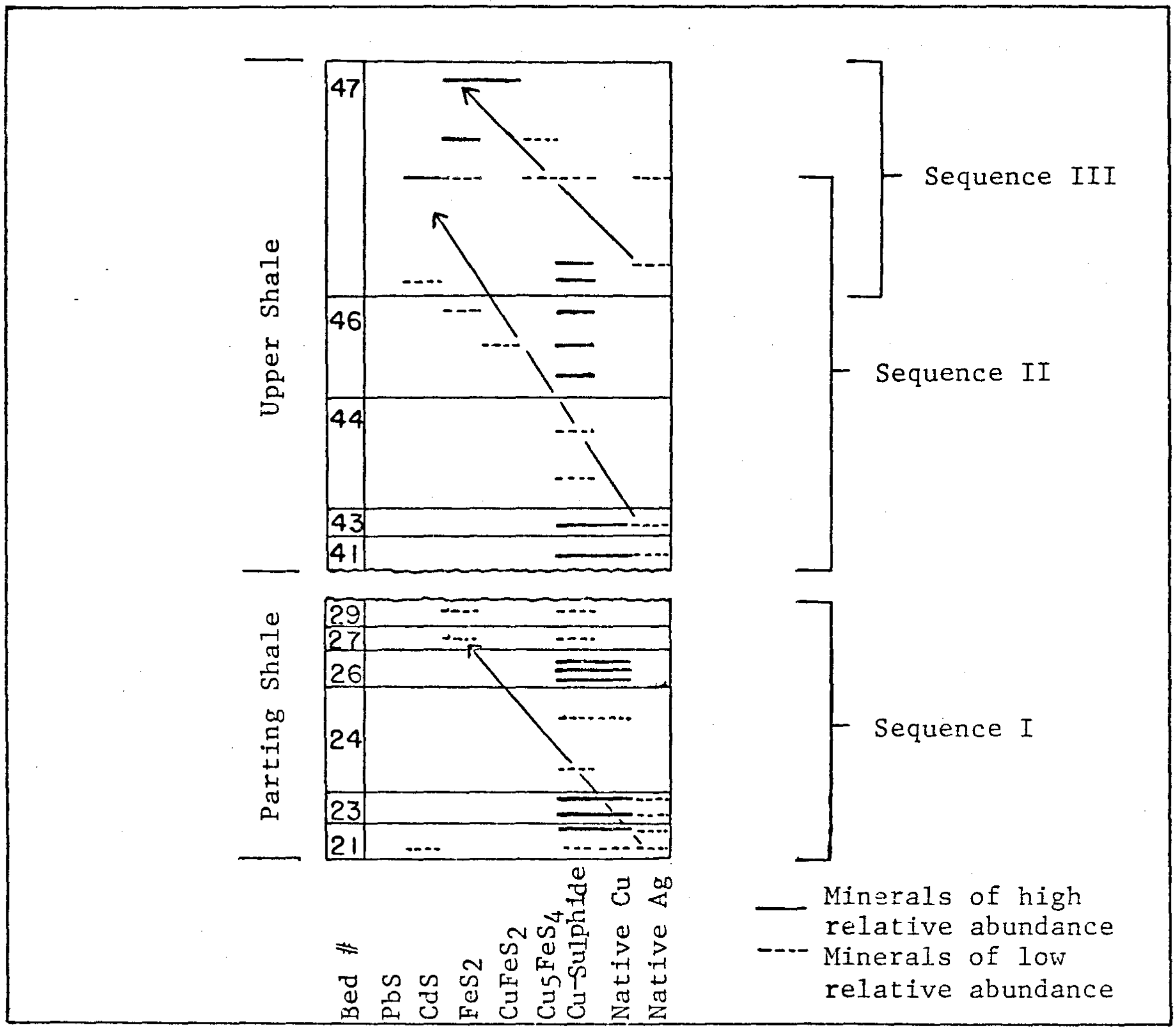
Native copper occurs within the interstices of the sandstone grains in the upper and lower sandstones. In the lower sandstone, native copper is found in close association with carbonaceous matter and chlorite, but replacing neither of these minerals (Hamilton, 1967). In this unit, native copper outlines quite well the cross stratification of the sandstones. Its distribution along the cross laminae appears to be a function of the distribution of organic carbon and the porosity of the sandstone (Hamilton, 1967). In the cupriferous zone of the Nonesuch shale, native copper can occur throughout the chalcocite-rich units, but may not always be present in these units as a result of the variability in the ore mineral zonation in the White Pine deposit. Native copper is probably about 7 to 9 x less abundant than chalcocite, as a whole, in the laminated siltstones and shales. In the same polished thin section, native copper generally has a larger grain size than nearby chalcocite.

Digenite, covellite, bornite, chalcopyrite, pyrite, greenockite, galena, cuprite and hematite have been identified and discussed by White and Wright (1954, 1966), Brown (1965, 1968) and Jost (1968). These minerals will be discussed in this thesis in so far as they occur in the mineralization sequences of the cupriferous zone.

(b) Mineral Zoning in the Cupriferous Zone

Jost (1968) has identified three mineralization sequences in the basal Nonesuch shale at the White Pine Mine. Each sequence is characterized by: 1) a decrease in the copper content of copper minerals in successively higher stratigraphic positions; 2) a gradual upwards decrease in the Cu:Fe ratio in copper iron sulphides; and 3) a decrease in overall copper mineral abundance with increasing stratigraphic position. Figure I-5 (Figure 4 of Jost, 1968) illustrates the three mineralization sequences within drill hole 33 - 3/8 F. The first sequence is contained entirely within the parting shale. Copper-rich lower units containing greenockite, pyrite, chalcocite-covellite-digenite, native copper and native silver pass upwards into copper-poorer units without greenockite or native silver and lastly pass into the uppermost #27 bed which contains only a few copper sulphides, copper iron sulphides and pyrite. In sequence II, like sequence I, greenockite, pyrite, copper sulphides and native silver occur in the lowermost units (#41 and #43 beds). Native copper does not occur here, but does in other profiles of the second sequence. This sequence ends in the upper part of the #46 bed with a decrease in the abundance of copper sulphides and the occurrence of copper iron sulphides. Sequence III, like the lower two sequences, shows zoning in ascending order from copper-rich minerals (Cu_2S, Cu_9S_5, CuS) to

Figure I -5: Mineral Zoning According to Jost (1968)



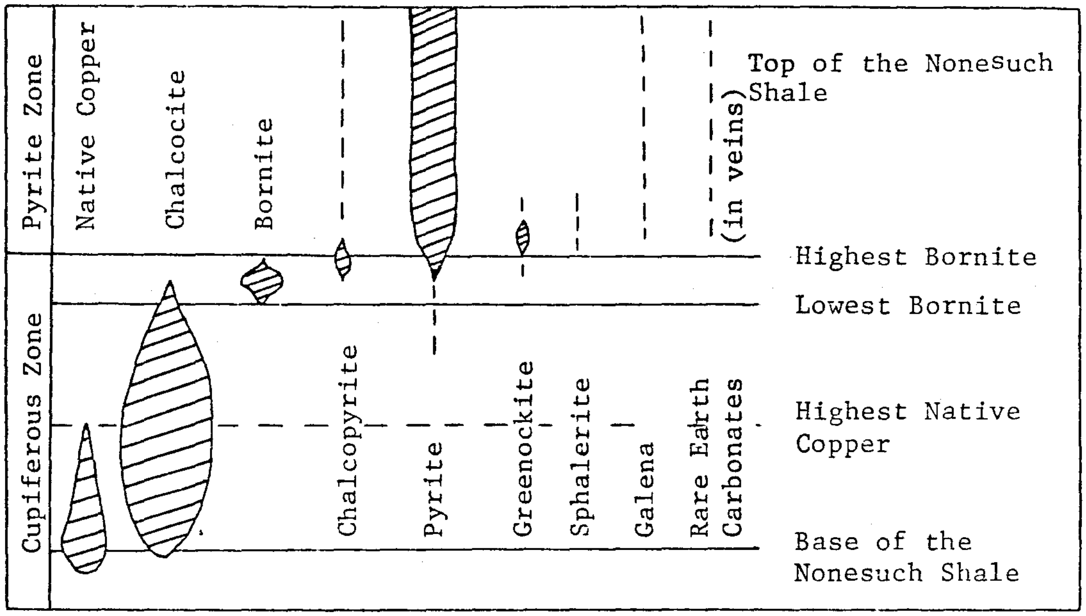


Figure I -6: Mineral Zoning According to White & Wright (1966) copper iron minerals (Cu_5FeS_4, $CuFeS_2$). Greenockite (CdS) is particularly abundant in the lowermost units of this sequence. Unlike the other two sequences, early pyrite is abundant and often appears to be replaced by later chalcocite, greenockite and chalcopyrite (Jost, 1968). These three sequences cannot be correlated over any distance within the cupriferous zone owing to the variability in type of mineralization, abundance of mineralization and the thickness of a sequence within a stratigraphic unit (Jost, 1968). Sequences II and III overlap to form a transition zone that marks an interval over which the upper part of sequence II has been enriched in copper by a later slight descending cementive copper mineralization that formed sequence III. This later mineralization is not considered as part of the cupriferous zone, and the top of the White Pine ore body can be placed in the upper part of the bornite-bearing unit which is approximately the upper boundary of sequence II (Jost, 1968).

In each of the upper and lower sandstones Jost (1968) has described a single copper mineralization sequence similar to the sequences in the overlying siltstones - shales, but in reverse order. That is to say, in the uppermost Copper Harbor conglomerate, the abundance of copper mineralization and the percentage of copper contained within the copper minerals decreases moving stratigraphically downwards from the contact with the overlying Nonesuch shale.

Brown (1965, 1968), and White and Wright (1966) recognize but one sequence of mineralization (see Figure I-6). The top of the cupriferous zone is defined by White and Wright (1966) as a surface "just above the stratigraphically highest bornite, where recognized, or just below the lowest greenockite or pyrite where no bornite is observed...". This surface has also been defined by these authors through the use of the 0.20% copper assay value. An equivalent surface, the fringe zone or transition zone has been defined by Brown (1968) as a zone a few inches thick marking the transition from the cupriferous zone to the overlying pyrite zone. The mineralogy of the fringe zone is distinct, when developed, consisting of the minerals, in ascending order: djurleite, digenite, bornite and chalcopyrite. In this zone, Brown also has observed the replacement of early pyrite by later copper minerals and has inferred that this was the cause of an ascending copper mineralization front. From mineralogical observations within drill cores and the use of the 0.20% Cu assay value, the top of the cupriferous zone has been traced and found to cross, at a gentle angle, the stratigraphic units within the White Pine Mine and Presque Isle areas (White and Wright,1966).

The mineral zone descriptions as given by Jost and by White and Wright and Brown differ as a result of the degree of detail and the areal extent of their studies. Jost by using the electron microprobe and a high power microscope has defined three mineralization sequences within the Nonesuch shale, each characterised by a decrease in the copper content of copper minerals in successively higher stratigraphic positions, by a gradual upwards decrease in the Cu:Fe ratio in the copper iron sulphides, and by a decrease in the overall copper mineral abundance with increasing stratigraphic position. Lower copper-rich units may or may not contain greenockite and pyrite. The more iron-rich and copper-poor upper units of a sequence usually contain pyrite. Jost's examination, however, was restricted to four complete profiles (drill cores) of the cupriferous zone. It may be a bit premature to apply the three mineralization sequences to the White Pine Mine as a whole in view of such a limited sample size. But, the mineral zone sequence does appear to be more complicated than that proposed by White and Wright (1966) and Brown (1965, 1968). Native copper is not restricted to the parting shale as proposed by White and Wright and Brown. It can occur as high as bed #47. Greenockite, pyrite and chalcopyrite are not restricted to the pyrite and transition zones. They do occur within the cupriferous zone as low as bed #23 (Jost, 1968). White and Wright and Brown's single mineral zone sequence refers to the most abundant occurrence of these minerals. Their examination outlined the transition zone in the White Pine and Presque Isle areas. Unfortunately their study relied heavily on the use of copper assay values and a 27 power binocular microscope. In view of the fine grain size of the White Pine ore a detailed examination of the ore microscopy such as that done by Jost must be completed over much of the White Pine deposit before an adequate mineral zone sequence can be defined.

(c) Structural Control of Mineralization in the Cupriferous Zone

Besides the previously discussed copper mineralization of the sandstones adjacent to the White Pine fault, numerous fractures and minor faults have been mineralized within the cupriferous zone at the White Pine Mine. The mineralization of these forms a very minor portion of the total mineralization of the cupriferous zone and it is distinctly later in time, than the dominant stratigraphically-controlled mineralization characteristic of the White Pine deposit. According to Carpenter (1963) the fracture-controlled mineralization is of two types: fracture-filled veins; and haloes. The mineralization in these veins is dominantly chalcocite, although a few veins contain native copper, native silver, blue chalcocite, covellite, bornite, chalcopyrite and pyrite. Carpenter (1963) ascribes the fracture-controlled mineralization to the leaching of mineralized rocks by and redeposition from low temperature, less than 105°C, hypogene solutions. A few of the mineralized veins may have been formed by the remobilization of sulphides into compaction fractures formed during the lithification of the sedimentary pile (Brown, 1968).

Section 8: Recent Mineralization Hypotheses

White and Wright (1966), Brown (1965, 1968) and D.E. White (1968) have suggested epigenetic mineralization hypotheses for the formation of the cupriferous zone at the White Pine Mine. White and Wright, and Brown have proposed that the cupriferous zone has been mineralized by ascending copper-rich solutions from the underlying Copper Harbor conglomerate. Ultimately these ore solutions may have been derived from the compaction of the Keweenawan sedimentary pile.* In this hypothesis, the ore solutions have replaced early biogenic-syngenetic pyrite prior to the lithification of these precupriferous zone pyritic Nonesuch sediments. Consequently the resulting copper sulphides have epigenetic cations but biogenic-syngenetic sulphur anions. The transition zone which marks the top of the present ore body has been interpreted as the furthest extent of the ascending copper mineralization front.

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* Elsewhere at the Calumet and Hecla mines, in the northern part of the Keweenaw penninsula, the middle Keweenawan Portage lava series contains economic native copper mineralization. Consequently, these lavas are an excellent source of copper for the Nonesuch shale mineralization.

According to D.E. White (1968) the cupriferous zone has been mineralized by the permeation of a copper-rich brine, in agreement with White and Wright, and Brown. However, in this hypothesis, the transition zone defines a density-controlled interface between an overlying water of normal density and an underlying heavy saline copper-rich ore fluid.

The bases of these epigenetic ore mineralization hypotheses are 1) good evidence, within the White Pine Mine, for the replacement of pyrite by copper sulphides; 2) a single ascending copper mineralization sequence ending with the occurrence of copper iron sulphides, greenockite and pyrite; and 3) the transgressive nature of the transition zone. However, evidence for the replacement of pyrite by copper sulphides is not common within the ore deposit, as a whole, and occurs only in a few parts of the transition zone. Furthermore, Jost (1968) has identified three copper mineralization sequences within the ore zone of the basal Nonesuch shale. A fourth similar but descending copper mineral sequence can be defined in the lower sandstone. Therefore if Jost's observations can be accepted as being generally applicable to the White Pine Mine, then the epigenetic mineralization hypotheses, as proposed, are untenable as an explanation for the mineralization of the cupriferous zone at the White Pine Mine.

Jost (1968) has proposed a syngenetic bacteriogenic ore mineralization hypothesis for the cupriferous zone. In this hypothesis, copper has been derived from the weathering and erosion of the copper-rich Portage lava series presumably exposed in the source area for the lower Nonesuch sediments to the south.* The type of ore mineral formed, and

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* The petrology of the lower and upper sandstones indicates a basic volcanic as a source rock (Jost, 1968; White and Wright, 1954)

its abundance is a function of the copper concentration in the sediment and pore fluids, the Cu:Fe ratio, the bacteriogenic sulphide concentration, the Eh-pH conditions within the sediments, and the stability constants of the sulphides. The I and II mineralization sequences (Jost, 1968) have been formed by the syngenetic - authigenetic precipitation of copper sulphides, first in the parting shale and later but partly contemporaneously, due to the fact that the bacteria would continue to produce sulphide within the lower beds even though overlain by several feet of sediments, within the second transgressive sedimentary interval the upper shale.

Earlier mineralization hypotheses are described in Butler and Burbank (1929), Nishio (1919), White and Wright (1954), and White (1960).

CHAPTER II

BIOGEOCHEMISTRY OF SULPHIDE

Section 1: Sulphide Producers (Types and Environmental Requirements)

Sulphides occurring in the reducing muds of many recent fresh water and marine environments have been precipitated by biogenic sulphide produced through the metabolic processes of the sulphate-reducing and proteolytic bacteria. The former group of organisms contains both assimilatory and dissimilatory varieties, of which the dissimilatory sulphate-reducers are more important with respect to the volume of sulphide produced. These dissimilatory bacteria do not retain the products of sulphate reduction within their bodies unlike the assimilatory organisms which reduce sulphate only in amounts necessary for the formation of amino acids and other sulphur-containing cellular components.

At present the known dissimilatory sulphate-reducing bacteria comprise the two genera *Desulphovibrio* and *Desulphotomaculum* which together contain 8 species (Postgate, 1959; Truper, 1969). So far, the 5 non-sporulating species of *Desulphobibrio* have been found in both marine and non-marine environments; however, the three sporulating species of *Desulphotomaculum* appear to be restricted to fresh water.

These dissimilatory bacteria are anaerobes which use sulphate as the terminal electron acceptor in their respiration. As the electron or hydrogen donor, molecular hydrogen or a variety of carbon compounds such as lactic, malic and formic acids, certain sugars or amino acids, and alcohols (ethanol, isobutanol, etc.) but not fatty acids including acetic acids may be used (Postgate, 1960 and Truper, 1969). These organic requirements are met in the lake bottom oozes, marine sediments and oil hydrocarbons of the natural environment. Bacteria of the genus Desulphovibrio are generally heterotrophic. However, Desulphovibrio desulphuricans makes hydrogenase and can therefore utilize molecular hydrogen in respiration and perhaps for autotrophic growth. The biochemical metabolic processes of the sulphate-reducing bacteria are not fully known, but can be summarized by the general reaction:

$$SO_4^{=} + (CH)_n \rightarrow H_2S + CO_2$$

The dissimilatory sulphate-reducers are anaerobes and therefore most active in an anoxic environment. Characteristic oxidation-reduction potentials and pH's for optimal activity are Eh = -100 to -200 mV and pH = 6.5 to 8.5. These bacteria have been found at Eh and pH extremes of respectively 100 and -400 mV (depending on the pH) and 4.5 to 9.8 pH units (Oppenheimer and Broneer, 1963; Truper, 1969).

Temperature requirements of the sulphate-reducing bacteria depend on the species. Desulphovibrio desulphuricans var. aestuarii are mesophiles showing good growth between 20° and 40°C. This temperature range applies to most marine Desulphovibrio strains. However, the spore-forming Desulphotomaculum nigrificans is an obligate thermophile growing best at 55°C. Sulphate-reducers have been reported in oil and sulphur wells at depths of 2000 to 4000 metres, growing in temperatures of 65° to 85°C under hydrostatic pressures of 200-400 atm. (Truper, 1969;

from Zobell, 1957).

Sulphate-reducers have been found in hypersaline, saline, and non-saline environments. Table II-1 (from Table 14, in Oppenheimer and Broneer, 1963) lists the NaCl tolerance of sulphate-reducing bacteria from various environments. Only Desulphovibrio desulphuricans var. aestuarii and Desulphovibrio salexigens are vitally dependent on the presence of NaCl. The former requires the Na^+ ion while the latter the Cl^- ion (Postgate and Campbell, 1966).

TABLE II-1: Salt resistance of sulphate-reducing bacteria from various habitat localities (Oppenheimer and Broneer, 1963)

Habitat of Sulphate-Reducing Bacteria	Salt resistance % NaCl
Soils and deposits of fresh water basins	0 to 1.5
Odessa harbors	8 to 30
Same	2 to 25
"	Up to 30
"	5 to 30
Oil Wells	Up to 18
Sea salt extractions	Up to 30
Sulphur deposits	6 to 13
Marine sediments	1.5 to 6
Ooze of marine canals	3 to 10
Mouths of rivers entering into the sea	Up to 30

Certain ions are required by the Desulphovibrio for their anaerobic functions. These are NH_4^+, Na^+, K^+, Mg^{2+}, SO_4^{-2}, Cl^-, CO_3^{2-} and $H_2PO_4^-$.

Ca^{2+}, Ba^{2+}, Mn, Fe^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Pb^{2+}, Cu, Hg^{2+} and Ag^{2+} depending and their concentration, are toxic to the sulphate-reducers. The order of increasing toxicity is Ca^{2+} to Ag^{+}. However, Fe^{2+} is vitally required by these bacteria, and in a concentration of 0.56 to 0.84 mg Fe^{2+}/litre for the optimum growth of the organism.

Sulphate-reducing bacteria are found abundantly within anaerobic sediments close to the water-sediment interface and in smaller numbers in the overlying water. The Black Sea serves as a good example. Here the sulphate-reducers are most abundant at the sediment-water interface and at a depth of 180m in the zone between overlying oxidized and underlying reduced water (Vinogradov et al, 1962). From Table II-2 below, an idea of the number of bacteria within sediments, and their variation with depth of sediment can be gained.

TABLE II-2: Vertical distribution of desulphurizing bacteria/ml in the sediments of some salt lakes (Oppenheimer & Broneer, 1963)

Depth of sediments (metres)	Umreschuo Lake (Eutrophic)	Mogilnoje Lake (Eutrophic)	Maibalyk Lake (Mesotrophic)	Repnoje Lake	Balkasch Lake containing Epsomite
0	1000	300	500	100,000	500
0.25	-	-	-	-	700
0.50	1000	100	30	-	500
1.0	-	10	60	100	-
2.0	-	-	100	100	-
3.0	-	-	-	1000	-
4.8	-	-	-	100	-
6.0	-	-	-	10	-
7.8	-	-	-	1	-

ZoBell and M. Skerman report respectively 10^3 to 10^4 and 10^5 sulphate-reducing bacteria/gram of sediment close to the water-sediment interface (Oppenheimer and Broneer, 1963).

Section 2: Biogenic Sedimentary Sulphides

Bacterial sulphate reduction and the concomitant production of hydrogen sulphide occurs in a very distinct sediment type. Such modern black, reducing marine muds contain no oxygen below the first 1cm or so of sediment, or may be reducing throughout, the reducing conditions extending into the water above. In the Lake of Faro (Sicily), reducing conditions extend some 20 metres above the sediment-water interface (S. Genovese, in Oppenheimer, 1963). The molecular diffusion of oxygen into these sediments is a slow process, and anaerobicity results from the *in situ* demand for oxygen exceeding the supply by diffusion. Most of the sulphate reduction in these sediments occurs in a zone immediately below the thin, 0 to 1cm, oxidized upper layer. The hydrogen sulphide produced can be fixed in the sediments by a reaction with iron to form a sulphide. Also, depending on the Eh and pH conditions of the sediments (respectively reducing and nearly neutral) part of the H_2S will dissociate to HS^-. Unreacted H_2S and HS^- can diffuse upwards to more oxidizing environments and be transformed spontaneously to sulphate, or be oxidized to native sulphur inorganically or biogenically by *Thiobacillus thioparus* and the coloured sulphur bacteria. Therefore, as proposed by Kanwisher and Östlund (in Jensen, 1962) very little H_2S can enter the atmosphere from these sapropelic muds.

In the recent sedimentary environment, only sulphides of iron have been well documented. Consequently, biogenic H_2S and HS^- will be retained within the sediment as the sulphide component of one of six iron sulphides. These are: greigite or cubic Fe_3S_4; mackinawite or tetragonal $Fe_{1+x}S$; amorphous FeS; pyrrhotite ($Fe_{1-x}S$); marcasite or orthorhombic

FeS_2; and pyrite or cubic FeS_2 (Berner, 1964, 1962, 1967). Greigite, mackinawite, and amorphous FeS are primary precipitates from the reaction of biogenic sulphides and iron, but they are thermodynamically unstable. In time, mackinawite and amorphous FeS will transform to pyrrhotite, and greigite to pyrrhotite and pyrite (Berner, 1967). The formation of pyrite involves the reaction of iron monosulphide (FeS) with native sulphur (Berner, 1962, 1970). This reaction is complete over a two year time period. The sulphide banding often observed in these sediments has been attributed to the relationship between the magnitude of the iron/sulphide ion ratio and the diffusion of iron and sulphide ions within the sediments (Berner, 1969). Occurrences of other non-ferrous biogenic sulphides have not been observed to any great extent in the recent sedimentary environment. Generally, bacteriogenically precipitated covellite, digenite, argentite, sphalerite, galena and chalcopyrite remain essentially laboratory curiosities of considerable theoretical value (Baas Becking and Moore, 1961; Temple and LeRoux, 1964). However, banded and disseminated sphalerite, chalcopyrite and pyrite have been well documented in the sediments from the deeps of the Red Sea (Degens et al, 1969). All three sulphides have been recorded in the cores from the Atlantis II deep. But, from a geochemical and sulphur isotopic study, it was determined that these sulphides represented syngenetic and epigenetic precipitates from a hydrothermal ore fluid. In the sediments from the Discovery deep, the only sulphides present are chalcopyrite and pyrite. The identification of sulphate-reducing bacteria in the sediments and the characteristic biogenic δS^{34} values of the sulphides substantiate a syngenetic-biogenic origin for these sulphides (Kaplan, Sweeney and Nissenbaum; in Degens, 1969).

Section 3: Bacterial Activity and Sulphur Isotopic Fractionation

An important geochemical aspect of the sulphate-reducing bacteria is their ability to fractionate sulphur isotopes. Pure cultures of *D. desulphuricans* under laboratory conditions can produce a maximum difference of -25 per mil between the sulphur isotopic composition of the heavy nutrient sulphate and the light metabolic hydrogen sulphide (Harrison and Thode, 1958; Kemp and Thode, 1968). From these laboratory studies definite empirical relationships have been derived between the magnitude of the isotopic fractionation and the parameters: sulphate concentration; type of electron donor; temperature; and rate of hydrogen sulphide production. At very low sulphate concentrations a small isotope effect has been observed, around 0 to 2 per mil (Jones and Starkey, 1957; Harrison and Thode, 1958; Kaplan and Rittenberg, 1964). Kemp and Thode (1968) observed that the isotope enrichments caused, at constant temperature, by *D. desulphuricans* were inversely proportional to the rate of sulphate reduction when ethanol and lactate were donors and directly proportional when hydrogen was the electron donor. At low temperatures, 11-20°C, in a lactate donor medium, resting cell suspensions of *Desulphovibrio desulphuricans* reduced sulphate at a rate which was directly proproportional to the amount of fractionation. This is the inverse of the relationship at temperatures above 24°C, the normal incubation temperatures of the bacteria (Kemp and Thode, 1968).

The 0 to 25 per mil isotopic fractionation values observed in the laboratory have been explained in terms of a general 5 step (see Table II-3) bacterial metabolic mechanism (Harrison and Thode, 1957; Kemp and Thode, 1968).

TABLE II-3:(From Kemp and Thode, 1968): The postulated five step Isotopic fractionation mechanism of D. desulphuricans

Step	Reaction
I	$H_2 + 2Fe^{3+} \xrightleftharpoons{\text{Hydrogenase}} 2Fe^{2+} + H^+$
II	$ATP + SO_4^{-2} \xrightleftharpoons{\text{ATP sulphurylase}} APS + \text{Pyrophosphate}$
III	$APS + 2Fe^{2+} \xrightleftharpoons{\text{APS Reductase}} AMP + SO_3^{2-} + Fe^{3+} + H_2O$
IV	$X + SO_3^{2-} \longrightarrow H_2S$
V	Assimilation of the electron donor

Steps I, II and V involve a small fractionation effect. However, steps III and IV involve larger fractionation effects of up to respectively 22‰ (Harrison and Thode, 1957) and 25‰ (Harrison, 1957). The isotopic composition of the metabolic H_2S will depend on which of steps I, II, III and V is rate-controlling, or on the degree of competition among these four steps. Step IV cannot be rate-controlling at any time since the reduction of sulphite to H_2S is too rapid. In experiments involving low sulphate concentrations, bacteriogenic H_2S showed a small isotopic fractionation of 0 to 2 per mil with respect to the del value of the sulphate (Jones and Starkey, 1957; Harrison and Thode, 1958). This can be interpreted as the result of step I, the assimilation of sulphate by the bacteria, having rate-control. Maximum fractionations of 23 to 25 per mil can be explained if step III is rate-controlling, while intermediate fractionations may be viewed in terms of the competition of steps I, II and V with step III for rate control (Kemp and Thode, 1968).

In the natural environment of both the present and the past, the value of $\delta_{\text{sulphate}} - \delta_{\text{sulphide}}$ is not restricted to 25‰. Fractionation effects of 10 to 62‰ have been commonly recorded for sulphides in marine and fresh water environments (Kaplan et al, 1963; Vinogradov et al, 1962; Kaplan et al, 1960; Kemp and Thode, 1968). Enrichments in S^{32} as great as 62 per mil suggest that the Kemp and Thode model for bacterial sulphur isotope fractionation is inapplicable to the natural environment or that some changes in this model must be made in order for it to apply to the natural environment.

Kemp and Thode (1968) discuss four main factors which can cause larger isotope fractionation effects than predicted by their five step mechanism. These factors are: open and closed systems; additive fractionation effects; alternate fractionation paths for D. desulphuricans; and sulphide production by chemical and other bacteriological processes.

In a closed system the sulphate supply available to the bacteria is very limited. The preference of the sulphate-reducer to utilize $S^{32}O_4^{-2}$ rather than $S^{34}O_4^{-2}$ in its metabolism results, in time, in the formation of a progressively heavier (more enriched in S^{34}) sulphate pool and progressively heavier hydrogen sulphide. This process is similar to a batch distillation or Rayleigh distillation effect, and a theoretical difference between $\delta S^{34}_{SO_4}$ and $\delta S^{34}_{H_2S}$, at 95% depletion of the sulphate supply, as great as 81.5‰ can be achieved (Kemp and Thode, 1968). The interstices of sediments and small lakes are examples of closed systems. Sulphate-reduction at the sediment-water interface, and within the water itself occurs in an environment of unlimited sulphate supply, or an open system. Here a fractionation effect of no greater than 25 per mil should occur.

A few additive fractionation effects are possible, and can produce S^{32} enrichments as great as 50 per mil. For example, a maximum kinetic isotope effect of 25‰ is possible in both the reduction of sulphate and sulphite (steps III and IV). If the reduction rate for both of these is equal, or the rate of the former greater than the rate of the latter, then these two fractionation factors may be additive. This effect has not been observed in the laboratory (Kemp and Thode, 1968). In the Black Sea at an interface 180m below the surface, biogenic hydrogen sulphide is oxidized to sulphur species such as sulphate (SO_4^-), sulphite (SO_3^{-2}) or thiosulphate ($S_2O_3^{-2}$). It is possible that the S^{32} enriched sulphite and sulphate can be reused by the sulphate-reducers, and consequently the 25 per mil fractionation factor could be compounded to produce a maximum isotope effect of 50 per mil. Further, unstable sulphur species such as sulphite and thiosulphate can undergo disproportionation reactions which involve a sulphur isotope fractionation close to 25 per mil (Granger and Warren, 1969). Therefore this disproportionation effect compounded with the biogenic fractionation factor could produce a fractionation effect as great as 50 per mil. These compound isotopic fractionation effects might explain the 50 per mil difference between $\delta S^{34}_{SO_4}$ and $\delta S^{34}_{H_2S}$ in the sea water. The difference can not be explained in terms of a closed system, since the sulphate supply is unlimited in the sea water medium (Kemp and Thode, 1968).

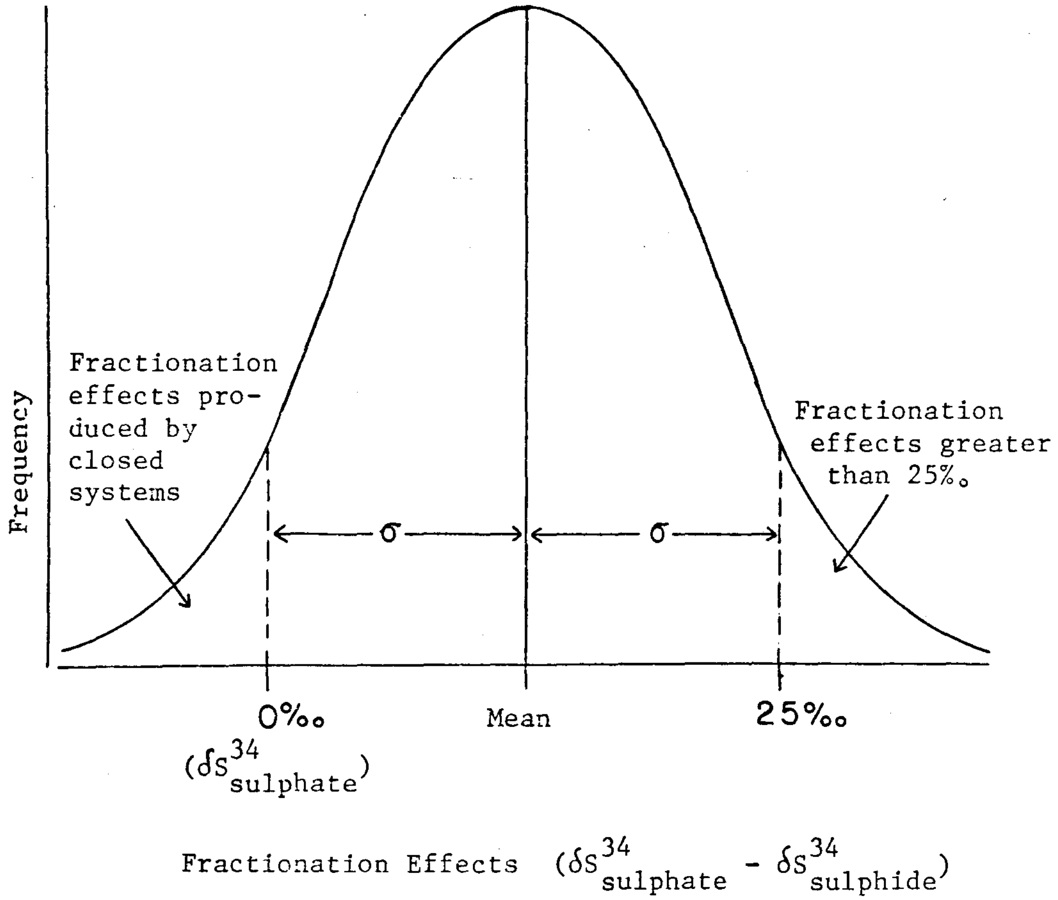
Under conditions unfavorable to normal metabolism, alternate pathways for sulphate reduction are available to certain organisms such as yeasts. Kaplan and Rittenberg (1964) found that such a pathway in yeasts produced sulphur isotopic enrichments of up to 41‰. Experiments have not yet been devised to demonstrate that for Desulphovibrio desulphuricans an alternate pathway exists with a fractionation factor greater than 25 per mil (Kemp and Thode, 1968).

Assimilatory sulphate-reducing organisms produce hydrogen sulphide only in small quantities. However, the proteolytic bacteria which produce H_2S from the break down of organic matter have been reported to be 100 to 1000 x more abundant than the dissimilatory sulphate-reducers in the sediments off the Texas Gulf Coast and Helgoland, Germany respectively (Gunkel and Oppenheimer; in Oppenheimer, 1963). Sulphur can be concentrated in plants in amounts ranging from 0.4 to 4.0% (Gunkel and Oppenheimer; in Oppenheimer, 1963). Therefore, depending on the amount of organic matter present in the sediment, a possibility exists for a significant sulphide contribution by these non-sulphate-reducing bacteria. The maximum S^{32} enrichment factor for the metabolic processes of the proteolytic bacteria has not yet been determined. If this factor is much greater than 25‰, even small quantities of sulphide from these bacteria may be important. Kemp and Thode (1968) consider the sulphide contribution from the proteolytic bacteria as minor but of undetermined quantity.

In conclusion, it can be seen that biogenic syngenetic sulphide deposits could be recognized, aside from their petrologic association with sedimentary rocks, by certain isotopic characteristics, namely: a wide range in δS^{34} (maximum $\delta S^{34}_{\text{sulphide}}$ - minimum $\delta S^{34}_{\text{sulphide}}$) values, ranges as great as 40 to 48 per mil have been reported for respectively the Kupferschiefer and the White Pine ore deposits; and a $\delta S^{34}_{\text{sulphide}}$ lighter than $\delta S^{34}_{\text{sulphate}}$ of contemporaneous sea water.

A third isotopic characteristic, the biogenic kinetic isotope fractionation factor may be a diagnostic feature of purely biogenic syngenetic sulphide deposits. Harrison and Thode (1958) and Kemp and Thode (1968) proposed that bacteria fradtionate sulphur isotopes over a range of fractionation effects ($\delta S^{34}_{\text{sulphate}} - \delta S^{34}_{\text{sulphide}}$) from 0 per mil to 25 per mil. Nakai and Jensen (1964) and Krouse and Sasaki (1968) have shown that fractionation effects as great as 40 per mil can be produced by bacterial action. Still larger fraction effects can be achieved by bacterial reduction of sulphate in a closed system. Consequently a purely biogenic syngenetic sulphide deposit will contain sulphides whose δS^{34} values will reflect any one or perhaps all three of these fractionation effects. If it can be assumed that the bacteria fractionate sulphur isotopes over a finite range of fractionation effects ($\delta S^{34}_{\text{sulphate}} - \delta S^{34}_{\text{sulphide}}$) and that part of this range is used more frequently by the bacteria, then a frequency distribution diagram of # of analyses vs. ($\delta S^{34}_{\text{sulphate}} - \delta S^{34}_{\text{sulphide}}$) should plot a curve that may be assumed to approximate a normal distribution. The preferred interval of fractionation effects should contain the majority of $\delta S^{34}_{\text{sulphide}}$ values. It has been assumed that this interval can be represented by twice the standard deviation (2σ) of the frequency distribution diagram. If this frequency distribution curve can be assumed to be normal, then 70% of the ($\delta S^{34}_{\text{sulphate}} - \delta S^{34}_{\text{sulphide}}$) values lie within this 2σ interval (1σ on either side of the mean value). It can be further assumed, in this model, that the upper boundary of this 2σ interval approximates the $\delta S^{34}_{\text{sulphate}}$ value of the sulphate supply used by the bacteria (see Figure II-1). If the Thode laboratory assumption of a common fractionation effect range of 0 to 25 per mil is nearly correct, then 2σ should be roughly 25 per mil. The 30% of δ values that lie outside of this 0 to 25 per mil range can be divided

Figure II-1: Statistical Model used to calculate $\delta S^{34}_{sulphate}$ for the Lower Nonesuch Shale



70% of the Data Lie within 1σ on either side of the mean.

into two groups. The first group consists of fractionation effects which are less than 0 per mil. This comprises about 15% of the data in the frequency distribution diagram. This group represents the fractionation effects produced by bacterial sulphate reduction in a closed system. The second group consists of fractionation effects greater than 25 per mil. This comprises about 15% of the data in the frequency distribution diagram. This group represents bacterial sulphate reduction using instantaneous fractionation factors greater than 25 per mil as proposed by Nakai and Jensen (1964) and Krouse (1968) (see Figure II-1).

Therefore if a sulphide deposit is sampled well enough, the calculation of 2σ of the $\delta S^{34}_{\text{sulphide}}$ values for the sample population may be an indication of a biogenic origin for the sulphide if 2σ is roughly 25 per mil.

CHAPTER III-A

THE GEOCHEMICAL PROBLEM

The White Pine ore deposit like most stratiform ore bodies, e.g. Mt. Isa, the Zambian Copperbelt, and the Recent Red Sea heavy metal deposits, has a controversial origin. As discussed in Chapter 1, there are two main mineralization hypotheses for the cupriferous zone. These are: 1) an epigenetic origin for the sulphides by an ascending copper-rich ore fluid; and 2) a biogenic syngenetic origin for the ore minerals. The former hypothesis has been based mainly on the cross-cutting nature of the transition zone and the apparent single Cu-rich to Fe-rich ascending metallic mineral sequence within the cupriferous zone (White and Wright, 1966; Brown, 1965 and 1968). Jost (1968) however, has shown that such a simple interpretation of the mineral zone pattern within the Mine is not possible. Further, it is my opinion that the transition zone is a diagenetic feature formed by the migration of slightly copper enriched porewaters outwards from the cupriferous zone during the compaction and dewatering of the already copper mineralized siltstones and shales. The copper within the porewaters was an excess that was not fixed by biogenic sulphide. It originated, as did the copper in the sulphides, from the clay minerals within the siltstones and shales (Jost, 1968).

This controversy over the origin of the ore mineralization, and of the significance of the transition zone could best be enlightened upon by adding to the too scant geochemical knowledge of the cupriferous zone. Consequently, a study of the sulphur isotopes, and carbon and sulphide contents in the sediments at the White Pine Mine, and a cursory examination of the boron content in the sediments of the pyrite and cupriferous zone was undertaken. Also, a study of the nature of the chlorite in the mineralized shales and siltstones and its relationship to the ore was begun in order to present a more complete picture of this proposed source for copper in the biogenic hypothesis. By choosing sample stations based on a three dimensional sampling grid it was hoped that the areal variation of $\delta S^{34}_{\text{sulphide}}$, weight per cent carbon and weight per cent sulphide, in the samples, would reflect the process of mineralization within the ore deposit

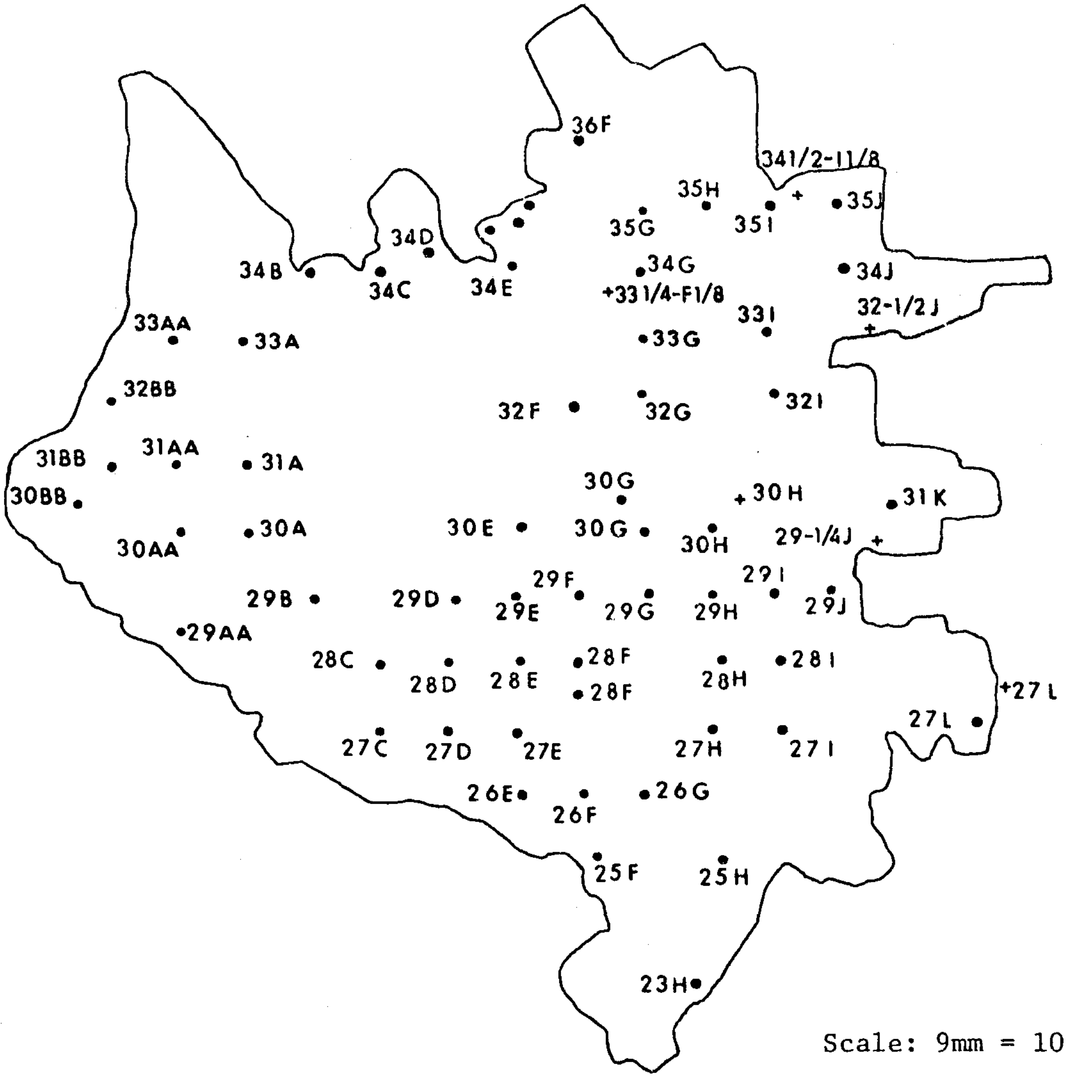
CHAPTER III-B

THE SAMPLING PROGRAMME FOR THE WHITE PINE MINE

The White Pine Mine was visited over a two week period beginning August 12, 1968. During this time, the lithology of the basal Nonesuch shale was studied, and 179 samples were collected for geochemical analysis. Samples were taken mainly from the #23, #26 and #43 units. A minor number of samples were taken from the #46 and #47 beds. In areas where all cupriferous beds are being mined several vertical sections, in which each unit of the cupriferous zone was sampled, were taken. Several partial vertical sections, in which every unit of the parting shale was sampled, were also taken.

Figure III-1

Sampling Pattern of the White Pine Mine



- • Sample Station
- \+ Drill Hole

Scale: 9mm = 1000 ft.

The sample stations were chosen from the grid pattern of the Mine map. Each 1000' square grid sector, labelled with a number and a letter, e.g. 29B or 30AA, was randomized using a table of random numbers. Grid sectors in areas of sand-fill and cave-in were eliminated from the sampling programme. Grid sectors were chosen until a good sample coverage of the mine was achieved. Samples were taken from the centre of each sector and labelled with a bed number and sector number. For example, sample #23-30A is a specimen from the #23 bed located at the centre of sector 30A. Due to recent sand-fill, cave-in and flooding, several samples were taken from stations not located at the centre of the mine sectors. The positions of the sample stations are illustrated in Figure III-1.

CHAPTER IV

GEOCHEMISTRY OF THE CUPRIFEROUS ZONE

Section 1: Sulphur Isotopes

(a) Method of Sulphur Extraction

Sulphur was extracted from powdered rock samples by a reaction with a reducing solution. A one to two gram sample of less than 150 mesh rock powder was placed in a flask containing 100 ml of a reducing solution made of HI, the active reducing agent, H_3PO_2 and HCl (see appendix I). The sample and reducing solution were boiled for a period of two to three hours within a semi-closed reflux system continually flushed with nitrogen gas. Sulphur was released from the sample as H_2S which was precipitated as CdS by bubbling the H_2S and nitrogen gas mixture through a cadmium acetate solution (see appendix I). This cadmium sulphide precipitate was then converted to silver sulphide (Ag_2S) by titration with a 0.5 N silver nitrate solution. Unfortunately, the reducing solution did not react specifically with sulphidic sulphur but converted sulphate and some organic sulphur to H_2S as well. Pyrite would not react with this solution.

Several 24 hour benzene soxhlet extractions, performed on powdered rock samples, indicated that the free sulphur and organic sulphur content in the lower Nonesuch sediments studied was negligible. Kaplan, Emery and Rittenberg (1963) also report negligible percentages of organic sulphur in the recent marine sediments off Southern California. Their analyses show that there is generally less than 0.01 weight per cent and no more than 0.03 weight per cent organic sulphur. According to Thode, Monster and Dunford (1958) as much as 12% sulphur can be extracted from some oils. Assuming that all of the organic matter in the lower Nonesuch shale is oil containing 12% sulphur, and that the reducing solution will liberate this sulphur, the greatest contribution of organic sulphur would be 0.13%. This is about 13% of the mean value for sulphide in the lower Nonesuch sediments at the White Pine Mine.

Qualitative tests for acid soluble sulphate using a 5% $BaCl_2$ solution were performed on 17 randomly chosen rock powders. No $BaSO_4$ precipitate was observed in the acid extracts of the samples. Forty polished thin sections were analysed under transmitted light using oil immersion and a magnification of 1250x. No positive identification of barium sulphate or any other sulphate mineral could be made. This is in agreement with Jost (1968) who analysed for barium in several polished thin sections from the lower Nonesuch using the electron microprobe.

A positive identification of pyrite could not be made in any of the polished thin sections studied for this thesis. However, a few 2-3 micron cubic ore minerals were observed, which may have been pyrite. Their abundance is so low and, in general, the abundance of pyrite in the copper mineralized portion of the lower Nonesuch shale is so low (White and Wright, 1954) that the pyrite sulphur contribution would be very small indeed. Therefore, any loss of sulphur in this analytical method due to the inertness of pyrite to the reducing solution was not considered as significant.

In view of the above discussions, virtually all of the sulphur extracted from the lower Nonesuch sediments, using the reducing solution method, is believed to be from the dominant ore mineral, chalcocite.

Initially acid soluble sulphide alone was extracted from the rock powders by boiling a 1 1/2 gram sample in 2:1 HCl. This method was discontinued because native sulphur was distilling onto the sides of the reflux condenser in the reduction apparatus. Tests using a 24 hour benzene soxhlet extraction could not detect any native sulphur in the rock samples which would sublime during the 2 hour boiling period in hydrochloric acid. The occurrence of native sulphur was probably the result of the spontaneous oxidation of hydrogen sulphide by an oxidized metal cation such as Cu^+, Cu^{2+}, or Fe^{3+}. This reaction is very probable in view of the mineralogy of the Nonesuch siltstones, and from a comparison of the standard oxidation potentials for the half cell reactions in Table IV-1 below. Therefore, a reduction in sulphide yield and an isotopic fractionation effect is possible.

TABLE IV-1: Standard oxidation potentials for sulphides, copper and iron half cell reactions

Half Cell Reaction	*E° (25°C)
$H_2S \longrightarrow S^\circ + 2H^+ + 2e^-$	-0.141 V
$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	-0.771 V
$Cu \longrightarrow Cu^+ + e^-$	-0.521 V
$Cu \longrightarrow Cu^{2+} + 2e^-$	-0.337 V

* From the Handbook of Chemistry and Physics (1963)

Experiments were done in order to test these two possible effects. Nine 1 1/2 gram rock powders from the #23 and #43 beds were each reacted with 2:1 HCl solutions for a period of 2 1/2 hours on the reduction apparatus. The weight per cent sulphur was determined for each sample, and the remaining HCl solutions were decanted from each of the reacted rock powder residues and tested for acid soluble sulphate. These rock powder residues were then reacted for 2 1/2 hours with the reducing solution. Sulphur contents were then determined for these nine sets of reductions. Nine corresponding rock powders which had not been pretreated with HCl were reacted with the reducing solution over the same time period, and sulphur percentages were determined for these samples. Table IV-2 presents the results from these experiments.

On the average, at least 32% of the sulphur within the rock powder remains unreacted using the HCl method. Part of this percentage may be due to the presence of organic sulphur, which may react in part only with the reducing solution, but on the whole, the unreacted sulphur is probably contained within composite gangue grains. The discrepancy between the per cent sulphur obtained by reacting the whole rock powder with reducing solution, and the per cent sulphur from the addition of columns 2 and 3, in Table IV-2, may be in part due to the reproducibility of the analytical method (± 0.02%).* However, most of the difference must be attributed to the loss of sulphur through the oxidation of H_2S by oxidized metal cations.

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* This estimate of reproducibility is the pooled standard deviation (see Dixon and Massey, 1957, p..109).

TABLE IV-2

Summary of results from experiments testing the amount of isotopic fractionation and reduction in sulphide yield using the HCl sulphide extraction method

1 Sample Number	2 % Sulphide 2:1 HCl treatment of rock powder	3 % Sulphide Reducing Soln. treatment of HCl pretreated rock powder residues	4 Total % S^{-2} (determined by adding across columns 2 and 3)	5 Fraction of Sulphide not liberated in the 2:1 HCl treatment	6 % Sulphide Reducing Soln. reaction with rock powder	7 Test for acid soluble sulphate	8 Per Cent difference between columns 6 and 4
23-30A	0.95%	0.41%	1.36%	0.30	1.74%	negative	22%
23-27E	0.87%	0.58%	1.45%	0.40	1.75%	"	22%
23-35I	0.75%	0.27%	1.02%	0.26	1.23%	"	17%
23-25F	0.79%	0.40%	1.19%	0.34	1.90%	"	37%
23-30H	0.55%	0.31%	0.86%	0.36	0.92%	"	7%
43-29H	1.60%	0.46%	2.06%	0.22	2.30%	"	10%
43-28I	0.96%	0.52%	1.48%	0.35	1.77%	"	16%
43-30G	0.60%	0.36%	0.96%	0.38	1.15%	"	17%
43-23H	0.89%	0.41%	1.30%	0.32	1.55%	"	16%
				Av = 0.32			Av = 18%

Table IV-3, below, lists the $\delta S^{34}_{\text{sulphide}}$ values obtained for the sulphides produced by a reaction of the whole rock powder with 2:1 HCl, for the sulphides produced by the treating of the HCl rock powder residue with the reducing solution and for the sulphides produced by reacting untreated whole rock powder with reducing solution. Samples 23-30A, 43-28I and 43-29H were chosen for analysis.

TABLE IV-3: A summary of results from experiments performed to determine the magnitude of sulphur isotopic fractionation in the oxidation of H_2S by oxidized metal cations

Sample Number	Sulphide Type	$\delta S^{34}_{\text{sulphide}}$ Values
43-29H	Rock Powder + 2:1 HCl	-9.33
	HCl residue + reducing solution	-9.56
	Rock powder + reducing solution	-9.41
43-28I	Rock powder + 2:1 HCl	-12.63
	HCl residue + reducing solution	-12.49
	Rock powder + reducing solution	-12.58
23-30A	Rock Powder + 2:1 HCl	+11.74
	HCl residue + reducing solution	+12.28
	Rock Powder + reducing solution	+12.20

Since the δ values for the three types of sulphides, in Table IV-3, are not appreciably different, there is no isotope effect involved in the oxidation of H_2S to native sulphur by oxidized metal cations. The similarity between the δ value of the sulphide extracted from the rock powder residue and the δ value of the sulphide from the HCl treatment of the whole rock powder indicates that no sulphur isotopic fractionation exists between the various sulphide components of the rock distinguished by their relative resistance to attack by HCl. Nevertheless, HCl treatment was stopped, and all ore powders were reacted with reducing solution.

(b) Sulphur Isotopic Analysis

The method for conversion of silver sulphide, from the reduction apparatus, to SO_2 gas, for mass spectrometric measurements, has been outlined by Thode, MacNamara and Collins (1949) and by Lusk (1968). This method involves the burning of 10 mg of pure sulphide at 1300 to 1400°C in a jet of preheated purified oxygen gas. The resultant gas is mainly SO_2 which was transferred by differential vacuum through a series of cold traps that removed any water vapor and CO_2. This purified SO_2 gas was then collected in a break-seal sample tube for mass spectrometric analysis.

A six inch, 90° gas source, simultaneous collecting, sample comparison mass spectrometer was used for SO_2 gas analysis. Results from this machine were recorded as $\delta_x^{L.S.}(66)^*$ values. These values were then corrected for oxygen, standardized to the Thode mass spectrometer and recorded as δS^{34} with respect to Park City Pyrite (P.C.P.) using the empirically derived equation $y = 0.906\ x - 0.3$ (1). In this equation y equals $\delta_x^{L.S.}(66)$, determined using the geology department mass spectrometer, and x equals $\delta_x^{PCP}\ S^{34}$ as would be determined from the Thode mass spectrometer and corrected for oxygen. The accepted δ value for PCP with respect to Canon Diablo Troilite (CDT) was determined to be +4.06 ± 0.2‰,

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* $\delta_x^{L.S.}(66)$ is the uncorrected per mil difference between the line standard (L.S.), P.C.P., and the sample (x).

respectively the mean and standard deviation of 17 analyses. By algebraically adding 4.06 to the x parameter of this equation, a very good approximation of δS^{34} value with respect to CDT was obtained (where $\delta_x^{CDT} S^{34}$‰ is defined as:

$$\delta_x^{CDT} S^{34}‰ = \left\{ \frac{\frac{S^{34}}{S^{32}} \text{ sample}}{\frac{S^{34}}{S^{32}} \text{ CDT}} -1 \right\} \text{x1000}).$$

This equation (1) was determined from a straight line fit to the data presented in Table IV-4. Henceforth, unless specifically stated, all δ values will be given as $\delta_x^{CDT} S^{34}$.

TABLE IV-4: Data from which the conversion equation from δ_x^{PCP}(66) to $\delta_x^{CDT} S^{34}$ was derived

Sample Description	Geology δ_x^{PCP}(66)	Thode Laboratory $\delta_x^{CDT} S^{34}$	*Thode Laboratory $\delta_x^{PCP} S^{34}$
Woods Hole Sea Water	+14.22±0.2%	+20.40±0.2%	+16.34±0.2%
Canon Diable Troilite	-4.14±0.2%	0.00±0.2%	-4.06±0.2%
Park City Pyrite	-0.38±0.2%	-4.06±0.2%	0.00±0.2%
23E-30E	-13.22±0.3%	-10.14±0.2%	-14.20±0.2%
23-27E	-9.77±0.2%	+15.23±0.2%	+11.17±0.2%
23-26G	+11.26±0.2%	+16.52±0.2%	+12.46±0.2%

* δ_x^{CDT} has been converted to δ_x^{PCP} by algebraically subtracting 4.06‰.

However, this is only an approximation. The correct equation for conversion is:

$$\delta_{x}^{PCP} = \delta_{x}^{CDT} + \delta_{CDT}^{PCP} + \frac{\delta_{x}^{CDT} \cdot \delta_{x}^{PCP}}{1000}$$

The value of +16.34 (from 20.40 - 4.06) for $\delta_{W.H.}^{PCP}$ sea water can be compared with the value of +16.18 determined using the conversion equation. These two values differ by 0.16‰, an amount which lies within the ±0.2‰ and ±0.3‰ error for the Thode and geology department spectrometers respectively.

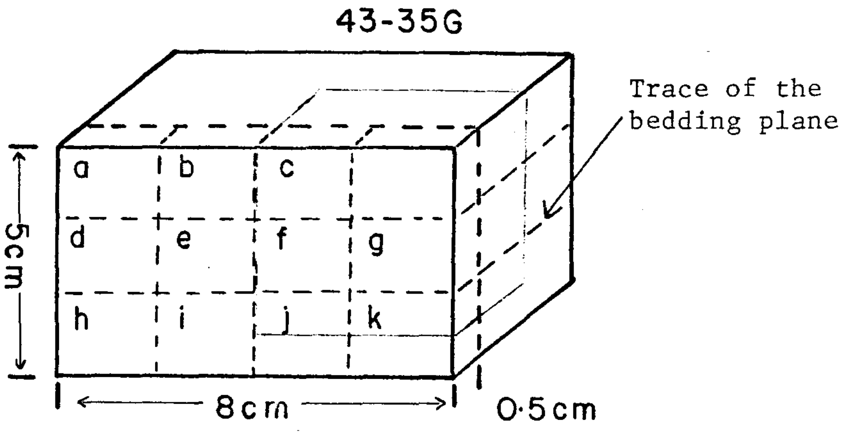
In order to estimate the variation to be expected in an analysis using the geology department mass spectrometer, 67 δ values were determined for the SO_2 line standard (see appendix IIb). These line standard analyses were interspersed throughout the determination of the δ values of the White Pine sulphides. The mean $\delta_{PCP}^{L.S.}$(66) of these 67 values is -0.38‰, the standard deviation is ±0.2‰ and the range is 1.08‰. The pooled standard deviation from 32 duplicate analyses of White Pine samples is ±0.3‰.

(c) Sulphur Isotopes of the White Pine Samples

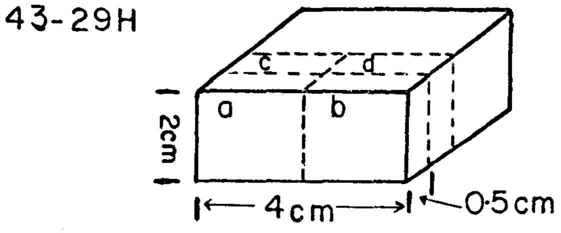
Fifty samples from each of the #23, #26 and #43 beds were collected for analysis. However, low sulphide contents in many of the samples, and lack of time resulted in isotopic analyses from only 39 samples in the #23 bed, and isotopic analyses of 24 samples in each of the #26 and #43 beds. A very few samples were obtained from the #47 and #49 beds, but due to the uncertainty in the position of the fringe zone at the time of sampling, sulphur isotopic analyses for these two units will not be included in this report. Seven analyses of the cupriferous zone close to the transition zone were obtained from drill core samples sent by the White Pine Mine. Pyrite mineralized samples from the overlying pyrite zone could not be obtained from the White Pine Mine in time for analysis.

Each δ value from the lower Nonesuch sediments represents an average for the sulphides contained within a rock specimen of approximate dimensions 4 cm x 4 cm x 1 cm. Some significance can be given to the δ values by determining the sulphur isotopic variation within a hand specimen. Figure IV-1 illustrates the subsampling pattern for three hand specimens from the #43 bed. Each of the alphabetically labelled subsamples have average dimension of 2 cm x 2 cm x 0.5 cm. The δ values for these subsamples are presented in Table IV-5. Comparing columns 3 and 5 of this table, the δ value determined from analysis of the rock powder from the standard sample size (4 cm x 4 cm x 1 cm) is in good agreement with the δ value calculated from averaging the isotopic analyses of the subsamples. The range in δ values for the sets of subsamples were considered in choosing the 5 per mil interval for the grouped data of the #23, #26 and #43 beds and of the cupriferous zone adjacent to the transition zone. Since these ranges (column 4, Table 5) are all greater than the average reproducibility of the mass spectrometer, ±0.3 per mil, there is a significant but small δ value variation within a hand specimen of the size used for sulphide extraction. A large spread in δ values such as the deposit exhibits as a whole is not reflected in a single hand specimen of the #43 bed.

Figure IV-1 Hand specimen sub-sampling patterns



Red inked block outlines the standard sample size that was crushed for analysis



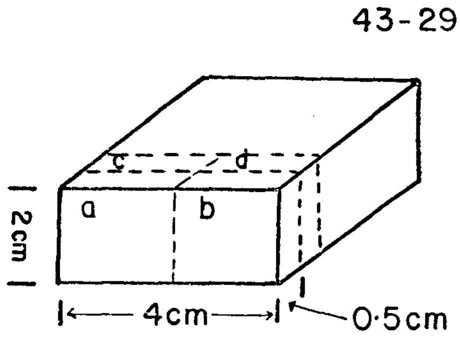


TABLE IV-5: δ value variation in hand specimens

	1	2	3	4	5
Sample Number	Sub-Sample	δS^{34} of sub-samples	Calculated average δS^{34} from the subsamples	Range of δS^{34} for the subsamples	δS^{34} from the Standard sample size
43-35G	C	-13.19‰	-11.92‰	4.85‰	-10.22‰
	D	-13.17‰			
	E	-12.44‰			
	F	-12.44‰			
	G	-8.34‰			
43-29H	A	-9.89‰	-10.26‰	0.72‰	-9.81‰
	B	-10.33‰			
	C	-10.61‰			
	D	-10.19‰			
43-29J	A	+3.62‰	+2.71‰	1.43‰	+2.17‰
	B	+2.19‰			
	C	+2.85‰			
	D	+2.19‰			

The larger range in del values for the subsamples of rock specimen 43-35G is probably related to its larger sample size.

Ungrouped $\delta S^{34}_{sulphide}$ values for the parting and upper shales of the lower Nonesuch are listed in appendix 2. These data have been grouped in 5 per mil intervals (Table IV-6) and are shown in histograms (Figures IV-2a, b, c, d and e). $\delta S^{34}_{sulphide}$ value means, ranges and standard deviations for the five stratigraphic units analysed are listed in Table IV-7.

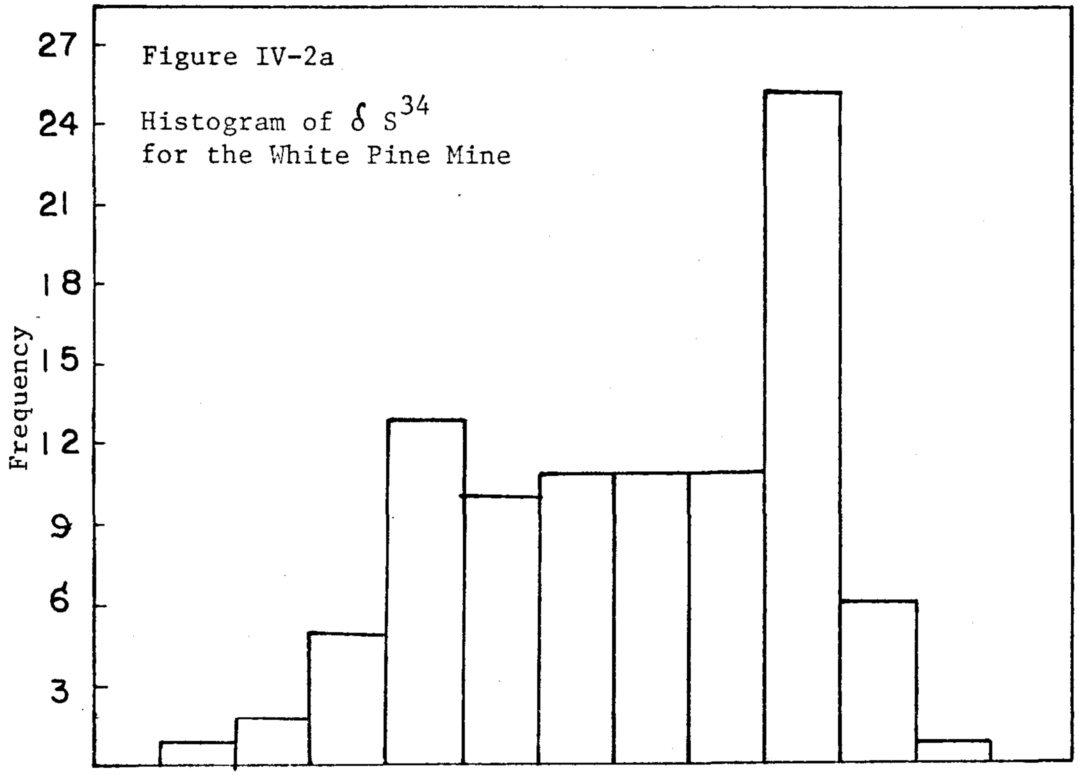


Figure IV-2a

Histogram of δS^{34} for the White Pine Mine

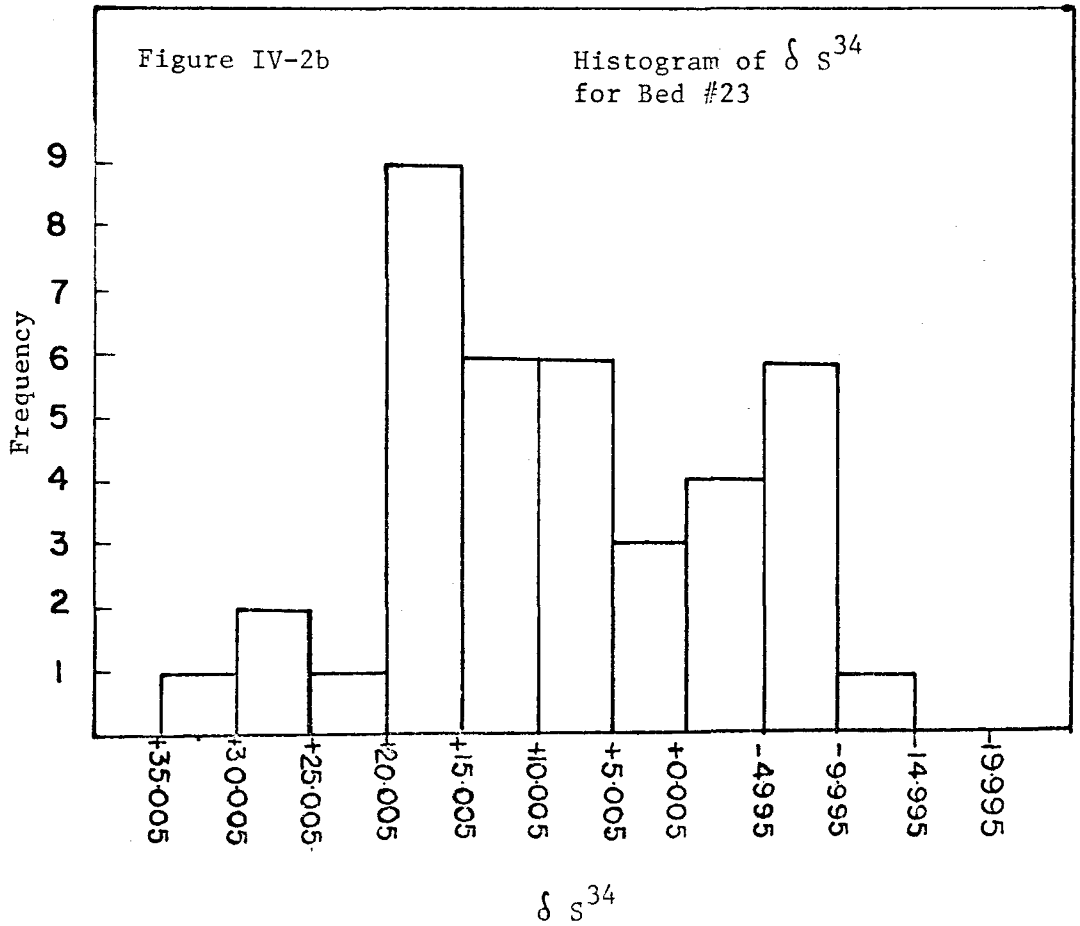


Figure IV-2b

Histogram of δS^{34} for Bed #23

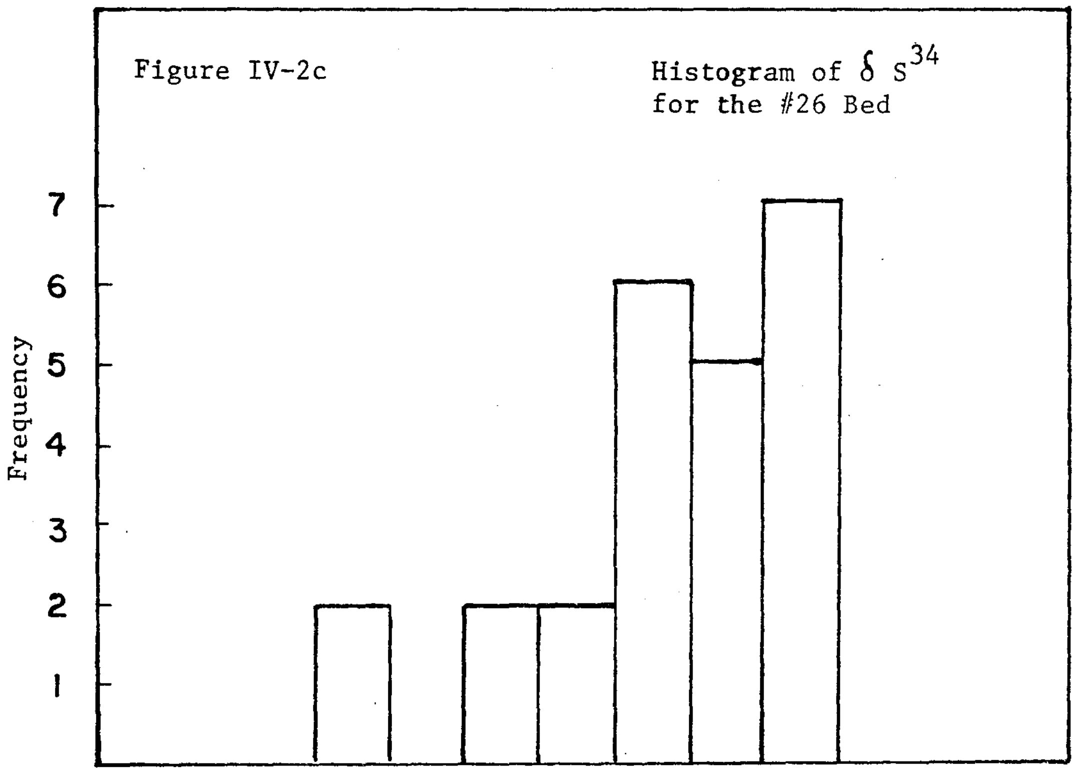


Figure IV-2c

Histogram of δS^{34} for the #26 Bed

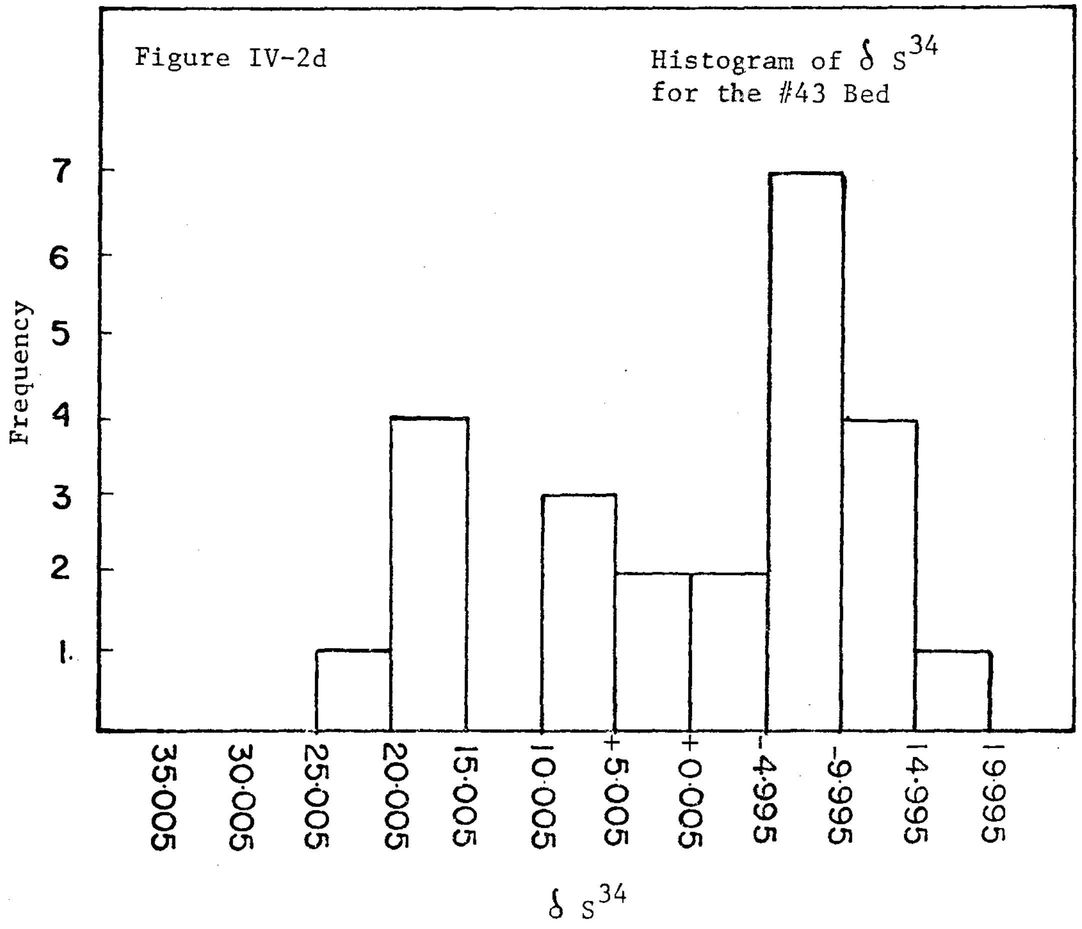


Figure IV-2d

Histogram of δS^{34} for the #43 Bed

Figure IV-2e

Histogram of δS^{34} for the cupriferous zone adjacent to the transition zone

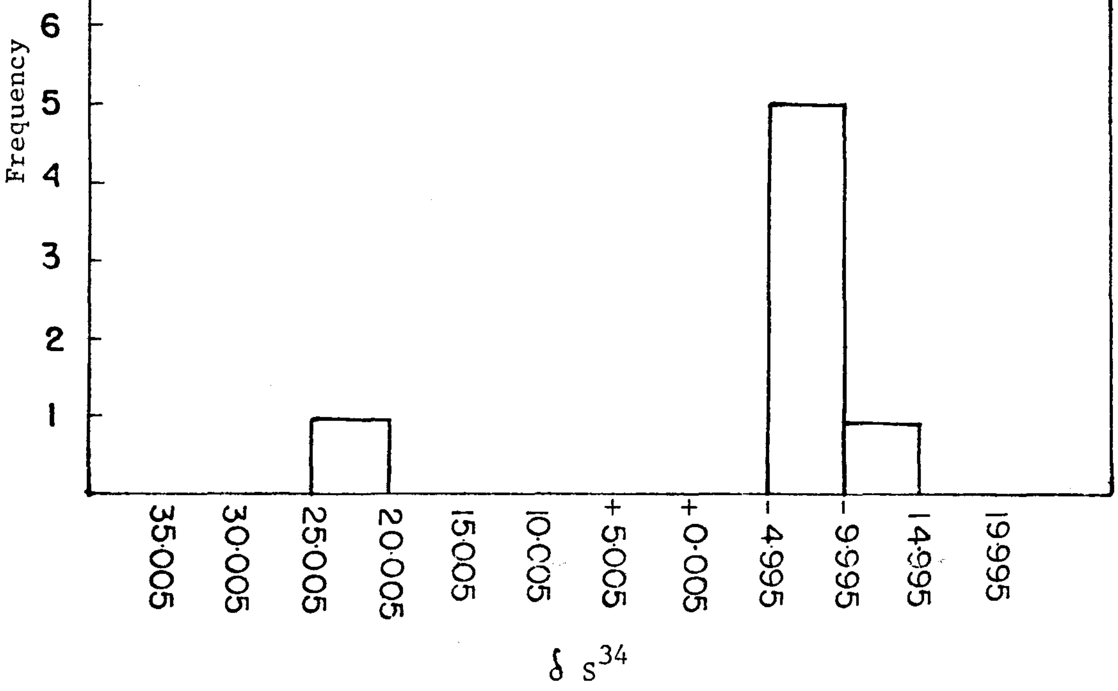


TABLE IV-6: Frequency tabulation of $\delta S^{34}_{sulphide}$

	Frequency		
Class Boundaries (‰)	White Pine Mine	Bed #23	Bed #26
+35.005 to +30.005	1	1	0
+30.005 to +25.005	2	2	0
+25.005 to +20.005	5	1	2
+20.005 to +15.005	13	9	0
+15.005 to +10.005	8	6	2
+10.005 to +5.005	11	6	2
+5.005 to +0.005	11	3	6
+0.005 to -4.995	11	4	5
-4.995 to -9.995	25	6	7
-9.995 to -14.995	6	1	0
-14.995 to -19.995	1	0	0
	94	39	24

	Frequency	
Class Boundaries	Bed #43	Cupriferous Zone Adjacent to the Transition Zone
+35.005 to +30.005	0	0
+30.005 to +25.005	0	0
+25.005 to +20.005	1	1
+20.005 to +15.005	4	0
+15.005 to +10.005	0	0
+10.005 to +5.005	3	0
+5.005 to +0.005	2	0
+0.005 to -4.995	2	0
-4.995 to -9.995	7	5
-9.995 to -14.995	4	1
-14.995 to -19.995	1	0
	24	7

TABLE IV-7: Mean, range and standard deviation (σ) for δS^{34} values from the White Pine Mine

Unit	1 Mean	2 σ	3 Range
White Pine Mine	+3.51‰*	11.70‰	48.29‰
Bed #23	+8.59‰	11.11‰	44.52‰
Bed #26	+1.32‰	9.20‰	32.87‰
Bed #43	-0.24‰	11.55‰	36.05‰
Cupriferous Zone adjacent to the transition zone	-4.41‰	12.87‰	35.35‰

* This mean value may be compared to the value of +5.9‰ determined from the mill concentrate by M.L. Jensen (reported by Wiese, 1960).

The wide range in del values (see Table IV-7, column 3) which both the individual units and the White Pine Mine as a whole exhibit, as well as the similarity of twice the standard deviation (2σ) of these units to the 25 per mil bacterial fractionation factor suggest that the sulphide is biogenic in origin (see Chapter II of this thesis). Further examination of the data in Table IV-7 and the histograms in Figure IV-2 reveals two trends. These are the tendency of the means to become more negative moving stratigraphically upwards from the #23 bed through the #26 bed to the #43 bed; and the tendency for the standard deviations of the #23, #26, and #43 beds to be similar. The cupriferous zone adjacent to the transition zone also follows these two trends. However, the few δS^{34} analyses for this zone (N=7) and the fact that the analyses were taken from samples representing different stratigraphic horizons, in keeping with the cross-cutting nature of the transition zone (see White and Wright, 1954; Brown, 1965 and 1968; and Jost, 1968), sheds doubt on the significance of this mean and standard deviation to the trends of the other lower units.

T tests (see Dixon and Massey, 1957, pp. 112-124) were performed on the means of the data for the #23, #26 and #43 beds and the cupriferous zone adjacent to the transition zone. Results are presented in Table IV-8. The null hypothesis that $\mu_1 = \mu_2$ was rejected at the significance level $\alpha = 0.10$ for the pairs Bed #23 - Bed #26, Bed #23 - Bed #43 and Cpz/Tz - Bed #23. The null hypothesis was accepted at this same level

TABLE IV-8: T test results from the comparison of the mean δS^{34} values from the #43, #26 and #23 beds and the cupriferous zone adjacent to the transition zone

Pair Tested	Calculated Test Statistic	Degrees of Freedom		Two sided test* critical values for the T distribution
#23-#26	2.66	61	0.10	1.671
#23-#43	2.99	61	0.10	1.671
#43-#26	0.464	46	0.10	1.680
**Cpz/Tz-#23	2.79	44	0.10	1.681
Cpz/Tz-#43	0.800	29	0.10	1.699
Cpz/Tz-#26	1.32	29	0.10	1.699

[*] From Dixon and Massey (1957), Table A-5, p. 384.

[**] Cpz/Tz: Cupriferous zone adjacent to the transition zone.

of significance for the pairs Bed #43 - Bed #26, Cpz/Tz - Bed #43 and Cpz/Tz - Bed #26. An estimate of the type II error (β) for $\alpha = 0.10$ was obtained from Table 12b in Dixon and Massey (1957). For the three pairs for which the null hypothesis was accepted, β was 60 to 90 per cent. For the three pairs for which the null hypothesis was rejected, $1 - \beta$ was 60 to 80 per cent. Therefore, the mean of the δS^{34} population for the #23 bed is significantly more positive than either of the means of the #26 and #43 beds, or the mean of the cupriferous zone adjacent to the transition zone. There are not enough data to test if the apparent tendency for the means of the δS^{34} sample populations to be progressively more negative going from the #26 bed to cupriferous zone adjacent to the transition zone, is statistically significant.

Table IV-9 contains the standard deviations for δ values from the sulphides of the #23, #26 and #43 beds as well as for the White Pine Mine as a whole. The similarity between twice the standard deviation (2σ) and the proposed common (0 to 25 per mil) fractionation effect interval for bacterial suplhate reduction (Harrison and Thode, 1958;

TABLE IV-9: σ and 2σ for the #23, #26 and #43 beds and for the White Pine Mine

Unit	Standard Deviation (σ)	2 x Standard Deviation (2σ)
Bed #23	11.1‰	22.2
Bed #26	9.2‰	18.4
Bed #43	11.6‰	23.2
White Pine Mine	11.7‰	23.4

Kemp and Thode, 1968) is significant. This fact suggests that the majority of δ values, about 70%, in the frequency distribution diagrams can be explained, theoretically, in terms of normal bacterial sulphate reduction. Therefore, the mean sulphate δS^{34} value of the lower Nonesuch paleoenvironment can be estimated as the upper boundary of the 25 per mil interval containing the most δ values. This value was determined to be $+15\pm2$ per mil which is the upper boundary of the 25 per mil interval containing the greatest cumulative percentage of δ-values for the White Pine Mine as a whole (see Table IV-10 and Figure IV-3). This $\delta S^{34}_{\text{sulphate}}$ is an average of the estimated $\delta S^{34}_{\text{sulphate}}$ values for the #23, #26 and #43 beds (see Figure IV-3). The $\delta S^{34}_{\text{sulphate}}$ values of the individual beds lie within a ±5 per mil range of this average value. Very similar $\delta S^{34}_{\text{sulphate}}$ values can be determined by algebraically adding the standard deviations of the #23, #26 and #43 beds and of the White Pine Mine as a whole to their respective mean $\delta S^{34}_{\text{sulphide}}$ values.

The $\delta S^{34}_{\text{sulphate}}$ value of $+15\pm2$‰ for the 1000 myr. Nonesuch paleoenvironment can be compared to the $\delta S^{34}_{\text{sulphate}}$ values for some Precambrian evaporites. Thode and Monster (1965) determined the $\delta S^{34}_{\text{sulphate}}$ for the 1000 myr. Grenville Balmat evaporites (New York) and for the greater than 635 myr. Proterozoic evaporites (Victoria Island, N.W.T. Canada) to be respectively +14.5‰ and +14.6‰. The similarity of the three $\delta S^{34}_{\text{sulphate}}$ values supports the 2σ hypothesis (see Chapter II-3).

It is possible to explain the more positive mean and mode of δS^{34} values in the #23 bed (see Figure IV-2) in terms of changes in the paleoecological conditions relevant to the metabolic activity of the Precambrian sulphate reducers in the lower Nonesuch paleoenvironment.

TABLE IV-10a: Data to calculate $\delta S^{34}_{\text{sulphate}}$

Upper Boundary of 25 per mil Interval	Cumulative Percents Bed #23	Bed #26	Bed #43	White Pine Mine
-19.995	0	0	0	0
-14.995	0	0	4.2	1.1
-9.995	2.6	0	20.8	7.5
-4.995	17.9	29.2	50.0	34.1
+0.005	28.2	50.0	58.4	45.7
+5.005	35.9	74.9	66.7	57.5
+10.005	51.3	83.3	79.1	69.1
+15.005	66.6	91.6	79.1	77.6
+20.005	89.7	91.6	95.9	91.5
+25.005	92.3	100.0	100.0	96.8
+30.005	97.5	100.0	100.0	99.0
+35.005	100.0	100.0	100.0	100.0

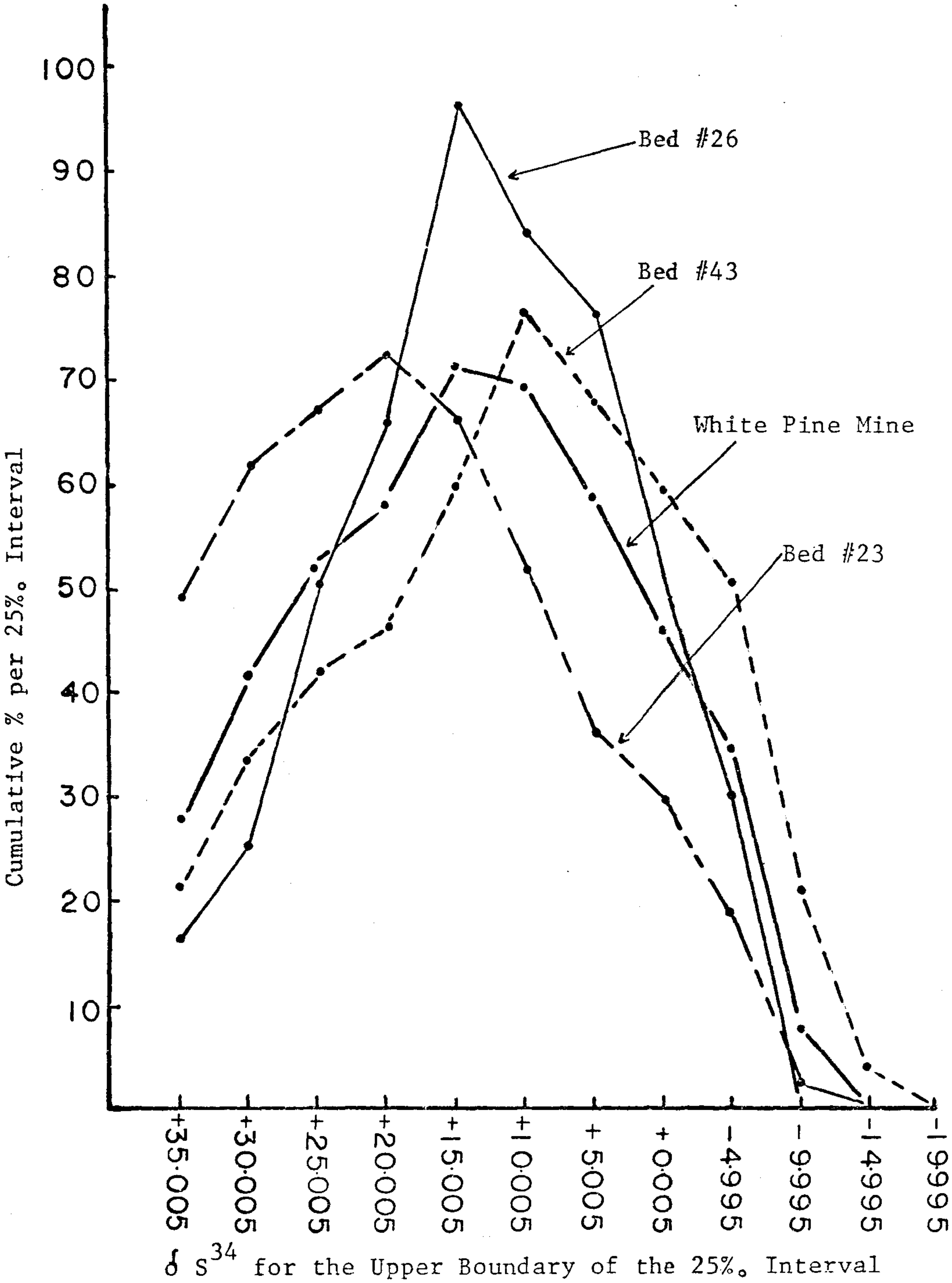
TABLE IV-10b: Data to calculate $\delta S^{34}_{\text{sulphate}}$

Upper Boundary of 25 per mil Interval	Cumulative Percents per 25 per mil Interval Bed #23	Bed #26	Bed #43	White Pine Mine
-19.995	0	0	0	0
-14.995	0	0	4.2	1.1
-9.995	2.6	0	20.8	7.5
-4.995	17.9	29.2	50.0	34.1
+0.005	28.2	50.0	58.4	45.7
+5.005	35.9	74.9	66.7	57.5
+10.005	51.3	83.3	74.9	68.0
+15.005	64.0	91.6	58.3	70.1
+20.005	71.8	62.4	45.9	57.4
+25.005	64.1	50.0	41.6	51.1
+30.005	61.6	25.1	33.3	41.5
+35.005	48.7	16.7	20.9	30.9

For an explanation see Figure IV-3

Figure IV-3

Plot of cumulative % per 25‰ interval vs. the δS^{34} for the upper boundary of the interval



Kemp and Thode (1968) have summarized a series of laboratory experiments in which factors affecting the metabolism of Desulphovibrio desulphuricans were changed. From these experiments the authors found that the enrichment of light sulphide and the rate of sulphate reduction varied. Kemp and Thode concluded that this variation in δS^{34} values could be explained in relation to the changes in environmental parameters through their postulated four-step bacterial sulphate reduction mechanism. However, it is uncertain how meaningful it is to apply the δS^{34}-environmental parameter relationships determined by Kemp and Thode (1968) in the laboratory to the paleoenvironment of the late Precambrian Nonesuch shale, or for that matter to the natural environment of today.

In the laboratory, Harrison and Thode (1958), and Jones and Starkey (1957) found minimal isotopic fractionation effects when the sulphate reducing bacteria were exposed to low sulphate concentrations. This effect would produce sulphides with a more positive δ value, approaching $\delta S^{34}_{\text{sulphate}}$ as a limit. These fractionation effects close to zero were explained by the authors as the result of the assimilation of sulphate by the cell controlling the rate of the reduction process. Consequently, the more positive mean and mode of the #23 bed could be explained by a decrease in sulphate concentration available to the bacterial population in the lower Nonesuch paleoenvironment. This decrease in sulphate concentration could have been achieved through an increasing influence of fresh water. The present mean sulphate concentration of fresh water from temperate climates is approximately 17 ppm (Hutchinson, 1967), while that of the ocean is about 2649 ppm (Krauskopf, 1967). Such a large difference as 156 x between the two sulphate concentrations can be compared to the difference of 17x used by Jones and

Starkey (1957) in their laboratory experiments. However, the sulphate concentration of fresh waters is variable on a world-wide scale (Data of Geochemistry). Consequently, sulphate concentration differences between present ocean water and fresh water as great as 200x and as small as 50x are possible. Furthermore, since the salt concentration in the ocean has evolved through time (Krauskopf, 1967) the application of these fresh water-salt water dilution factors to the uppermost Precambrian must be done only very qualitatively. Evidence for a fresh water influence in the upper Keweenawan lower Nonesuch paleoenvironment is found in the sedimentology (White and Wright, 1954), the paleontology (Moore et al, 1969) and the geochemistry (discussion on boron, this thesis, IV-section 4). Nakai and Jensen (1960) report fractionation factors of 1.005 to 1.007 for bacterial sulphate reduction in fresh water muds.

The range of δS^{34} values in beds #23, 26 and 43 (see Table IV-11) exceeds the 25 per mil maximum fractionation factor characteristic of normal bacterial sulphate reduction. One explanation for this is that portions of the paleoenvironment of these three beds were closed systems (see Chapter II-3 of this thesis) with respect to sulphate transfer. Since the sulphate supply is limited in such a system a process similar to a batch type distillation can be initiated by the sulphate reducers. As a result, the $\delta S^{34}_{\text{sulphate}}$ value of the sulphate pool becomes more positive and the biogenic sulphides become progressively heavier. Therefore the more positive $\delta S^{34}_{\text{sulphide}}$ mean and mode of the #23 bed as well as the larger range and larger positive δ values than either the #26 or #43 beds may be explained in terms of a tendency for this bed to contain systems which were more closed; that is to say, systems that underwent a greater depletion of sulphate supply than either of the other two overlying beds. The systems were probably closed either during the active sedimentation of the corresponding units through the influence of environmental barriers, or later as the units were gradually removed from the sulphate supply by burial. The inferred influence of fresh water in the lower Nonesuch paleoenvironment would increase the possibility of generating closed systems with greater percentages of sulphate depletion through the large dilution factor involved.

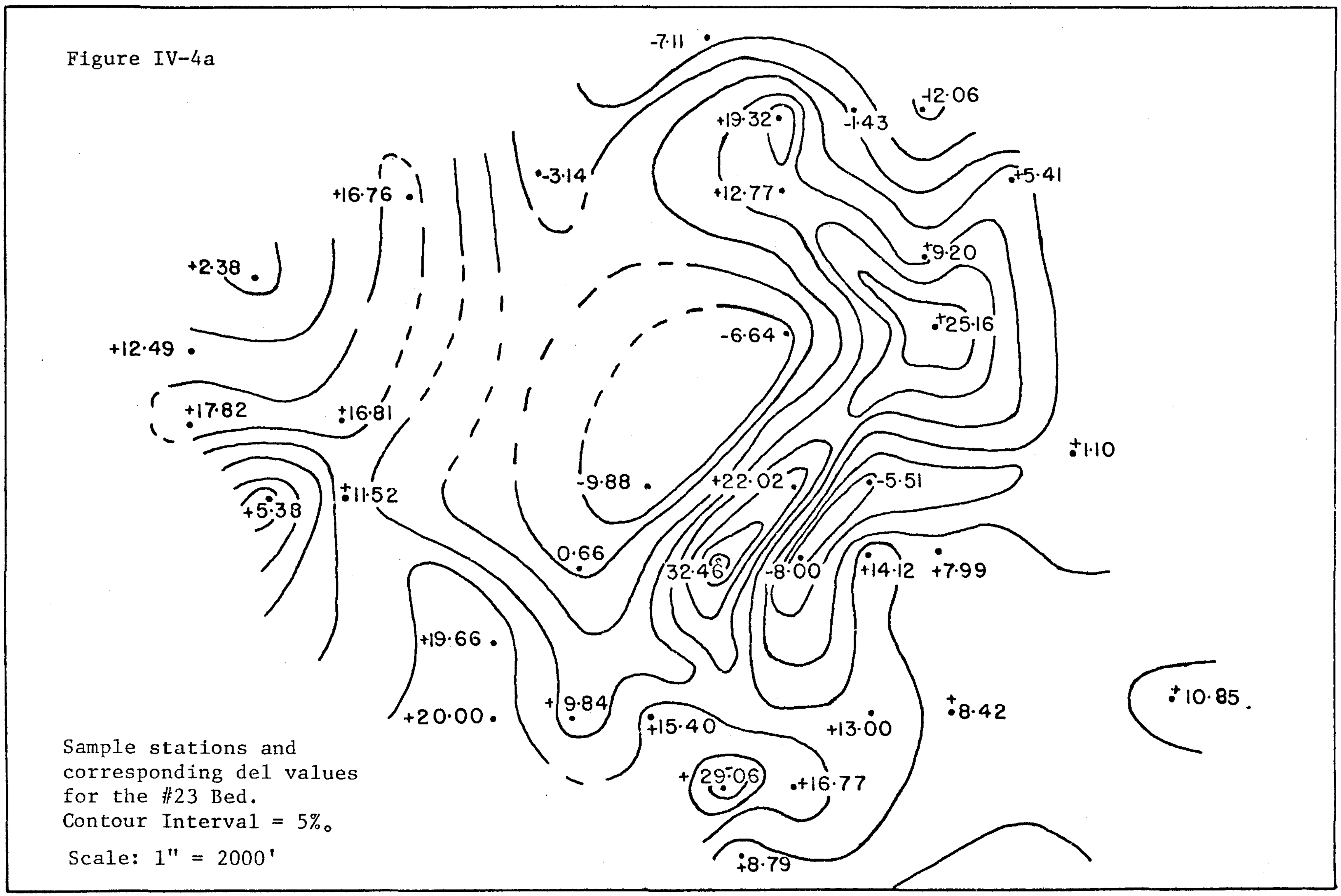
TABLE IV-11: The range in δS^{34} and sample size for the #23, #26 and #43 beds

Stratigraphic Unit	Minimum δS^{34}	Maximum δS^{34}	Range	Sample Size
Bed #23	-12.06‰	+32.52‰	44.52‰	39
Bed #26	-9.67‰	+23.20‰	32.87‰	24
Bed #43	-15.83‰	+20.22‰	36.05‰	24

(d) Areal Variation of δS^{34} values

Figures IV-4a, b, c show the sample location and corresponding δ value for beds #23, #26 and #43 respectively. These diagrams have been contoured by hand using 5 per mil intervals. It has been assumed that the samples in each unit were taken from the same stratigraphic level within the unit. This in fact was not the case and the samples could vary in stratigraphic position within a unit by as much as 1 1/2 feet. Figures IV-4a and 4c show distinct areas of high and low δ values and well developed contour trends of respectively N.E. to S.W. and N.N.W. to S.S.E. These trends show conspicuous parallelism with the isopach

Figure IV-4a



Sample stations and
corresponding del values
for the #23 Bed.
Contour Interval = 5‰

Scale: 1" = 2000'

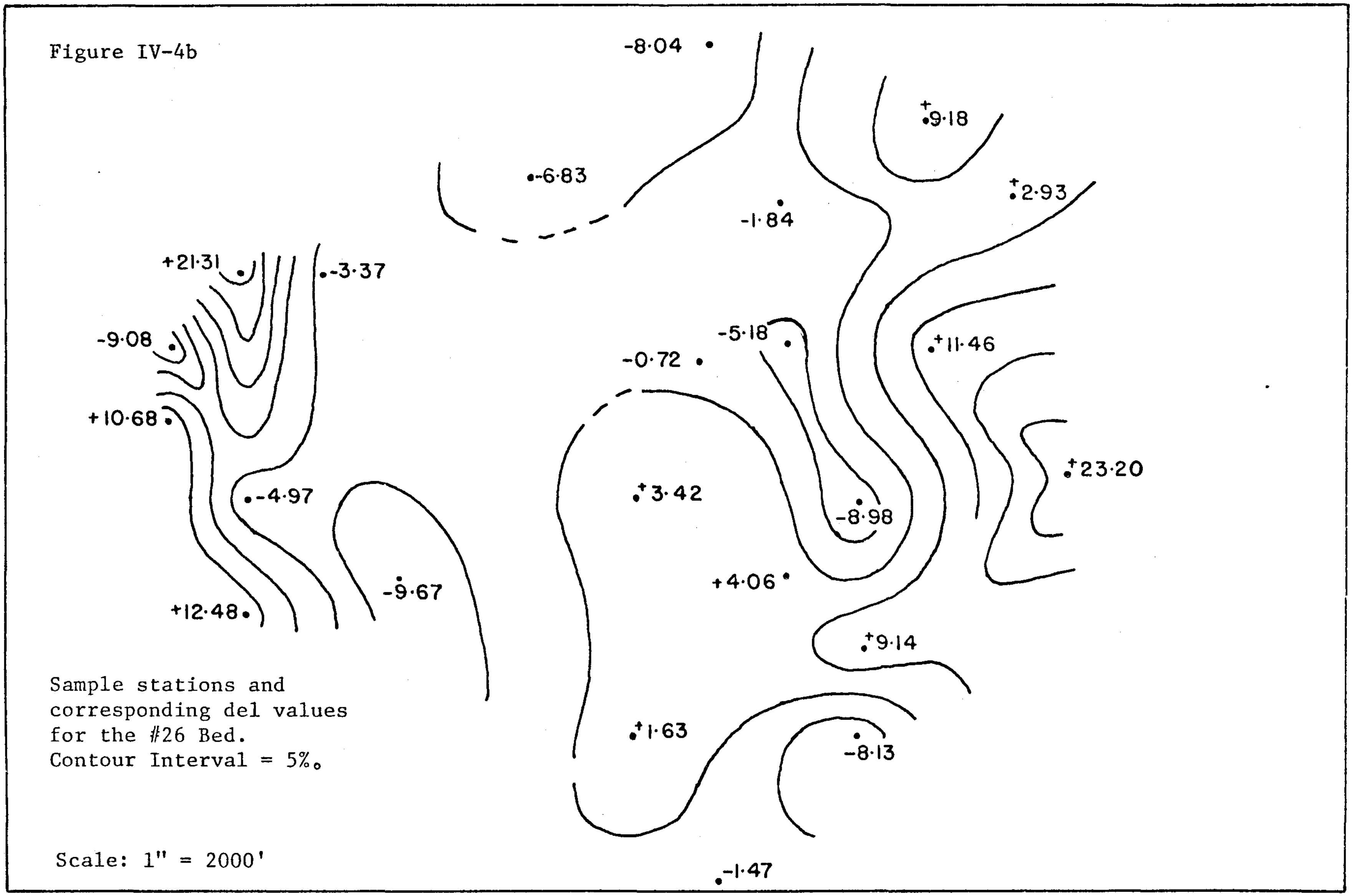
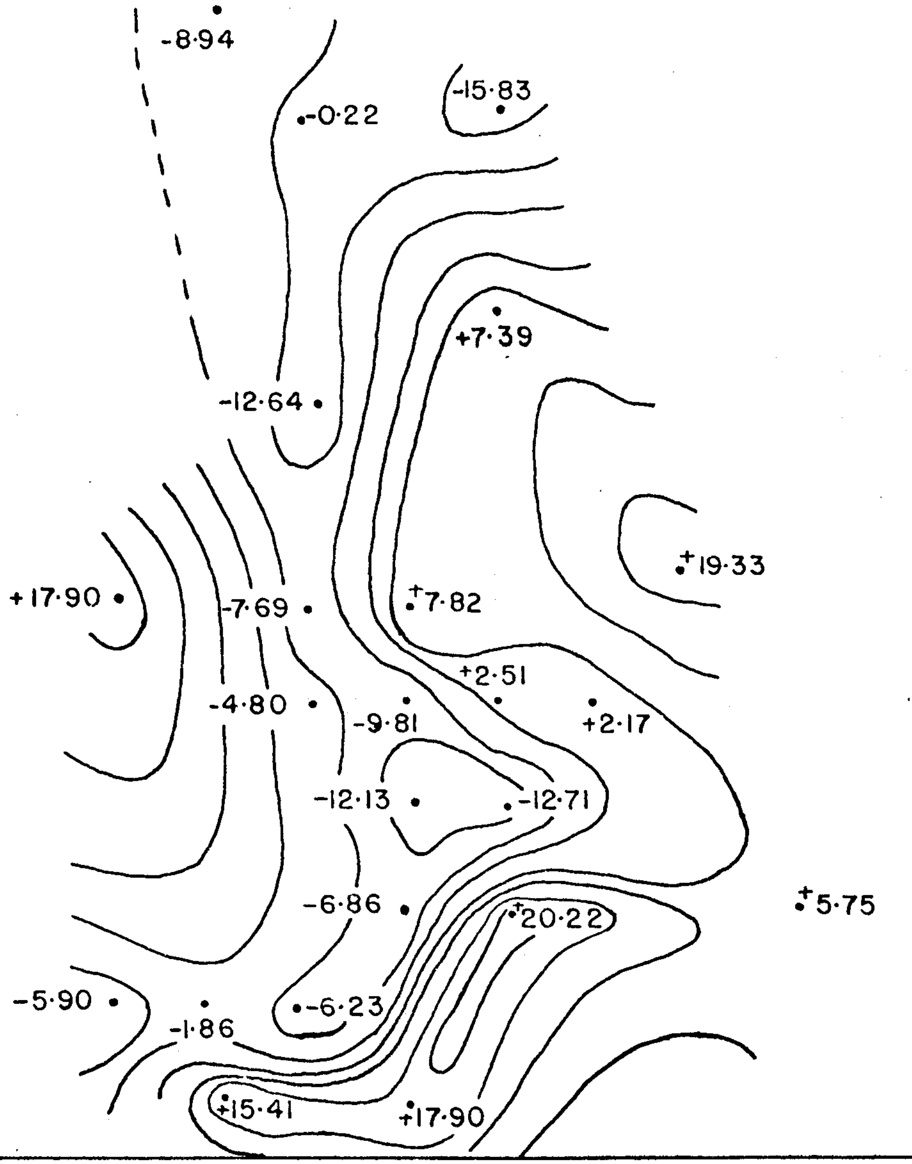


Figure IV-4b

Sample stations and
corresponding del values
for the #26 Bed.
Contour Interval = 5‰

Scale: 1" = 2000'

Figure IV-4c



Sample stations and
corresponding del values
for the #43 Bed.
Contour Interval = 5‰

Scale: 1" = 2000'

and copper grade trends for the #23 and #43 beds suggested by White and Wright (1954). A more detailed analyses of δ values together with sulphide per cent-contour trends and their significance to the lower Nonesuch paleoenvironment can be found in section 3 of this chapter.

Section 2: Total Carbon Analysis

(a) Method of Analysis

Finer than 150 mesh whole rock powders were analysed for carbon using a Cenco induction furnace carbon analysis apparatus. In this method, one quarter of a gram of rock powder was placed in a magnesium oxide refractory crucible and mixed with a conductor, high purity iron filings, and a catalyst, tin coated copper pellets. Samples were burned in pure oxygen releasing CO, CO_2, and SO_2. Carbon monoxide was converted to carbon dioxide on a platinum catalyst while sulphur dioxide was absorbed on MnO. The amount of CO_2 in the sample was measured by volume loss using a KOH solution absorbant. Analyses were recorded as a volume change, corrected for temperature and barometric pressure and converted by slide rule to weight per cent carbon. A single analysis takes, on the average, 8 minutes.

Table IV-12 lists duplicate or triplicate analyses of eight samples. The pooled standard deviation (Sp) of these analyses (see Dixon and Massey, 1957, p. 109) was calculated in order to estimate the error of the method of analysis. This error is ±0.03 weight per cent.

Any carbonate present in the rock will also be liberated in this procedure. However, Brown (1968) found that the amounts of carbonate in the samples of the cupriferous zone that he analysed were small, 0.009 to 0.020 weight per cent. These figures are in agreement with the qualitative tests for carbonate done on many of the ore samples for this thesis. Therefore the total carbon analyses listed in appendix III are fairly good approximations of the organic carbon content of the samples.

TABLE IV-12: Replicate carbon analyses used to estimate the pooled standard deviation

Sample #	Analysis #1	Analysis #2	Analysis #3
Gr. Std. #3a	0.130%	0.148%	
Iron Std. 19G	0.239%	0.204%	0.240%
Iron Std. 12Ha	0.462%	0.461%	0.454%
Iron Std. 122D	3.33%	3.29%	
43-23H	0.616%	0.640%	
23-34D	0.27%	0.28%	
23-33AA	0.15%	0.18%	
23-32G	0.53%	0.48%	

(b) Results and Discussions

Carbon analyses for the #23, #26 and #43 beds and for the cupriferous zone adjacent to the transition zone are listed in appendix 3. Histograms of carbon analyses are presented in Figures IV-5a, b, c, d, and e. These figures together with Table IV-13 show a small but general increase in mean weight per cent carbon moving stratigraphically upwards from the #23 bed through the #26 bed to the #43 bed. The standard deviation of the #26 bed is small in comparison to the standard deviations of the #23 and #43 beds (see Table IV-13). This may be the result of the apparently unrelated more massive and more uniform lithology of the

Figure IV-5a

Histogram of the weight % carbon for the White Pine Mine

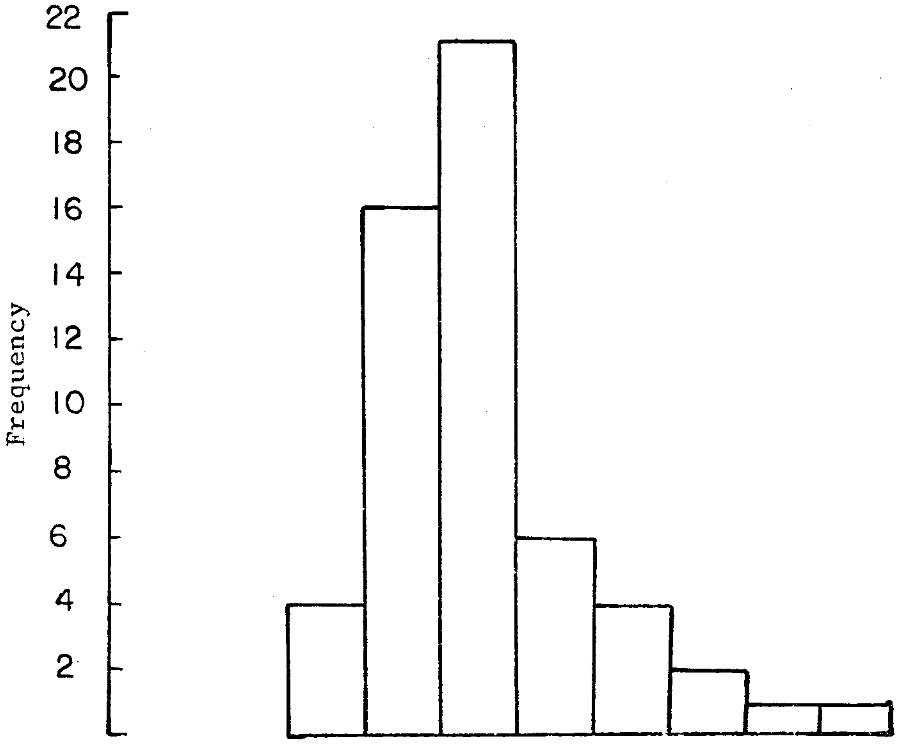


Figure IV-5b

Histogram of the weight % carbon for the #23 Bed

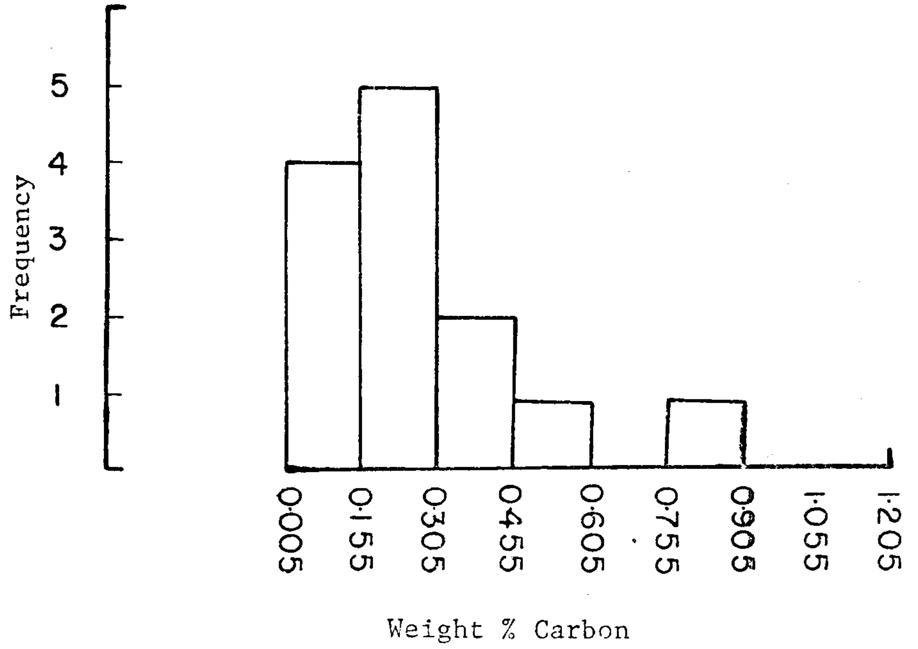


Figure IV-5c

Histogram of the Weight % carbon for the #26 Bed

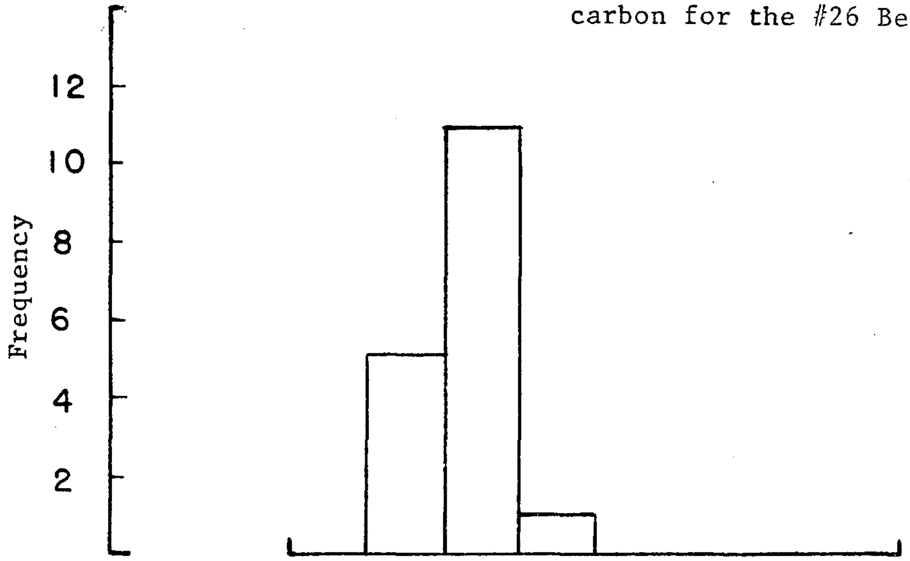


Figure IV-5d

Histogram of the Weight % carbon for the #43 Bed

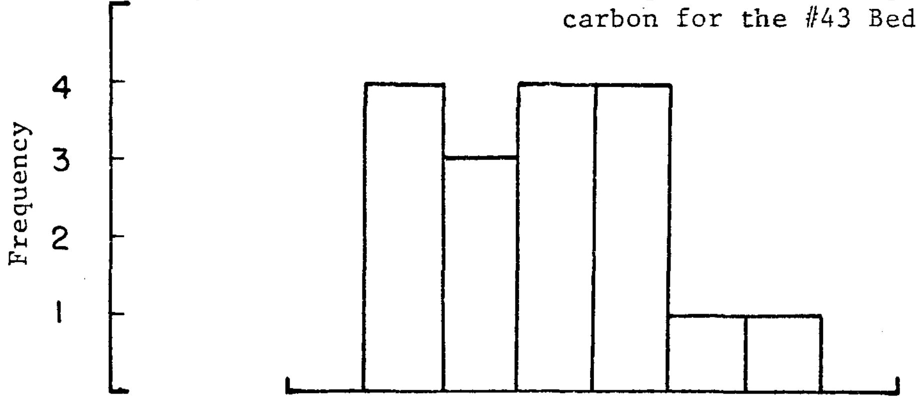
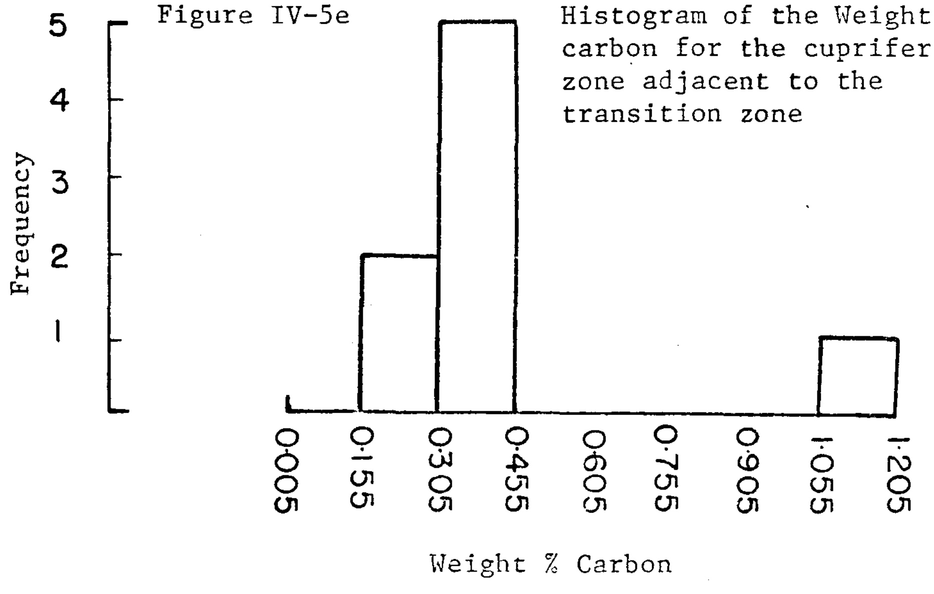


Figure IV-5e

Histogram of the Weight % carbon for the cupriferous zone adjacent to the transition zone



#26 bed, or perhaps due to the fact that carbon, as petroleum, can be a mobile component and therefore capable of evening out its concentration by migration within this siltstone unit.

TABLE IV-13: The mean and standard deviation for weight % carbon in the units of the White Pine Mine

Stratigraphic Unit	Mean weight % Carbon	Standard Deviation (σ)	Sample Size
Bed #23	0.300%	0.214%	13
Bed #26	0.337%	0.074%	17
Bed #43	0.510%	0.242%	17
*Cpz/Tz	0.447%	0.301%	8
White Pine Mine	0.398%	0.221%	55

* Cpz/Tz designates the cupriferous zone adjacent to the transition zone.

The mean weight per cent carbon in each of the units suggests about 2 volume per cent organic matter in the White Pine Mine. This agrees with what can be seen in thin section.

The total carbon analyses determined in this thesis are in good agreement with Vine _et al_ (1969) and Brown (1965, 1968) who report values for organic carbon of, respectively, less than 0.01 weight per cent up to 0.9 weight per cent for the striped unit (#61 bed) and 0.11 to 0.39 weight per cent for the cupriferous zone adjacent to the transition zone. Total carbon is an important environmental parameter of the lower Nonesuch shale since it is probably a measure of the Eh of the paleoenvironment and of the nutrient available to the sulphate reducers.

Section 3: Sulphide Analysis

(a) Method of Sulphide Analysis

The weight per cent sulphide was determined from the weight of sulphide, precipitated as Ag_2S, extracted from the whole rock powder for isotopic measurement (see section I-a of this chapter). Since the weight of rock powder reacted with the reducing solution and the weight of Ag_2S precipitated were accurately known, it was a simple matter of determining the weight per cent sulphide in the rock specimen. It was assumed that the silver sulphide was stoichiometric, and that the yield of the reduction apparatus was 100%. In fact, the yield was slightly less than this, about 97%. The error in this method has been estimated as the pooled standard deviation of 9 sets of duplicate analyses (see Table IV-14; and Dixon and Massey, 1957, p. 109). This estimate of error is ±0.02 weight per cent.

TABLE IV-14: Duplicate analyses of sulphide % used to calculate the pooled standard deviation (Sp).

Sample Number	1st Analysis % S^{-2}	2nd Analysis % S^{-2}	Range	Estimated Variance (σ^2)
23-30AA	1.97%	2.00%	0.03%	0.000404
23-26F	0.27%	0.27%	0.00%	0.000000
23-32I	0.28%	0.30%	0.02%	0.000179
23-30H	0.92%	0.93%	0.01%	0.00045
23-29I	0.32%	0.32%	0.00%	0.000000
26-31BB	0.27%	0.29%	0.02%	0.000179
43-29J	1.32%	1.33%	0.01%	0.000045
43-28I	1.77%	1.74%	0.03%	0.000404
43-29H	2.30%	2.21%	0.09%	0.003626
				$Sp^2=5.42\times10^{-4}$

(b) Results and Discussions

Sulphide analyses for the #23 bed, #26 bed, #43 bed, the cupriferous zone adjacent to the transition zone and for the White Pine Mine as a whole are presented in appendix 4. Histograms of these data together with means and standard deviations are illustrated in Figures IV-6a, b, c, d, and e. The means of the sulphide data for the #23, #26 and #43 beds agree in trend with the average Mine copper grades for these units. That is, these three units can be placed, with respect to copper grade, and per cent sulphide in the following descending order: bed #43, bed #23 and bed #26. The mean sulphide per cent for the cupriferous zone adjacent to the transition zone is of uncertain significance. This is the result of having too few data and the samples being collected not from one stratigraphic unit, but from three, namely the #46, #44 and #43 beds.

(c) Areal Variation of Weight Percent Sulphide, and its Relationship to δS^{34}

Figures IV-7a, b, c indicate the areal distribution of sample localities and corresponding sulphide percentages within the White Pine Mine for the #23, #26 and #43 beds respectively. The sulphide percentages have been contoured by hand using 0.3% intervals. Although there are too few data points for good contour control, there is a definite north to south trend for beds #23 and #43 (see Figures IV-7a and 7c). This trend agrees in general direction with the trends of the contoured δ values for bed #43 and to a lesser extent for bed #23. By superimposing the contoured sulphide diagram for bed #43 (Figure IV-7c) over the corresponding contoured δ value diagram (Figure IV-4c) a marked correlation can be shown to exist between maximum sulphide percentages and minimum δ

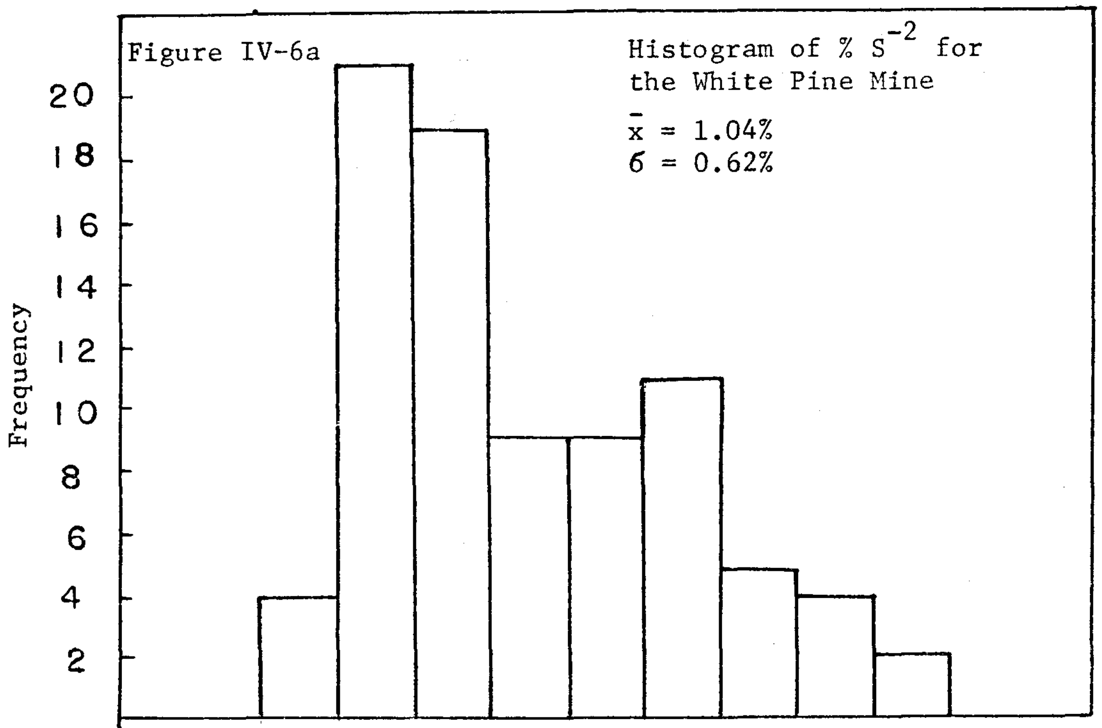


Figure IV-6a

Histogram of % S^{-2} for the White Pine Mine

$\bar{x}$ = 1.04%

σ = 0.62%

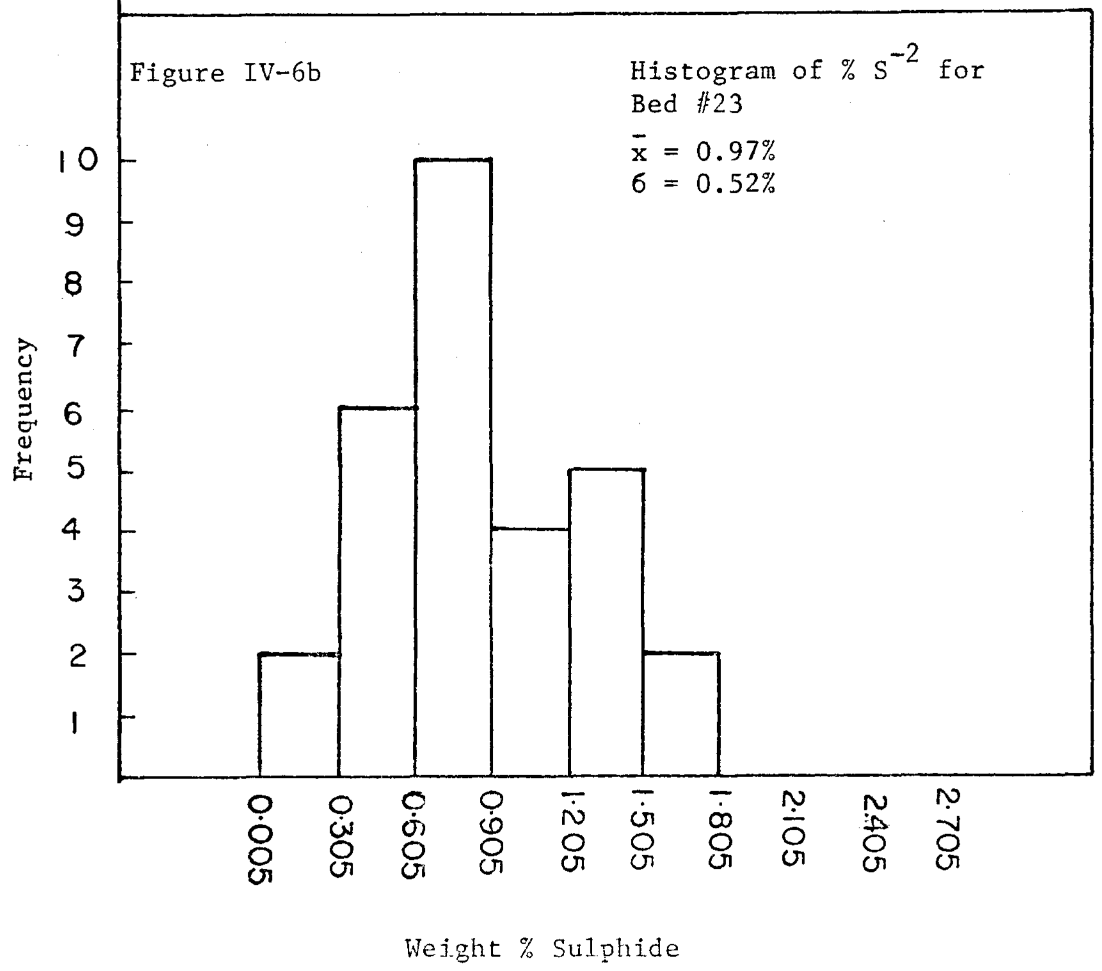


Figure IV-6b

Histogram of % S^{-2} for Bed #23

$\bar{x}$ = 0.97%

σ = 0.52%

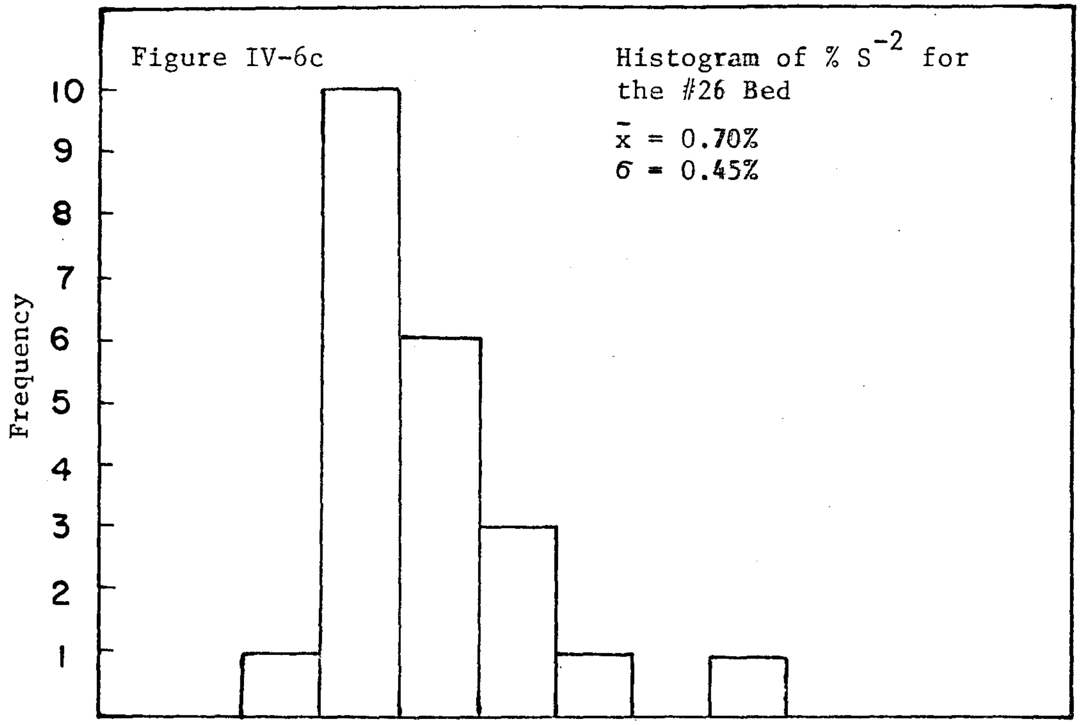


Figure IV-6c

Histogram of % S^{-2} for the #26 Bed

$\bar{x}$ = 0.70%

σ = 0.45%

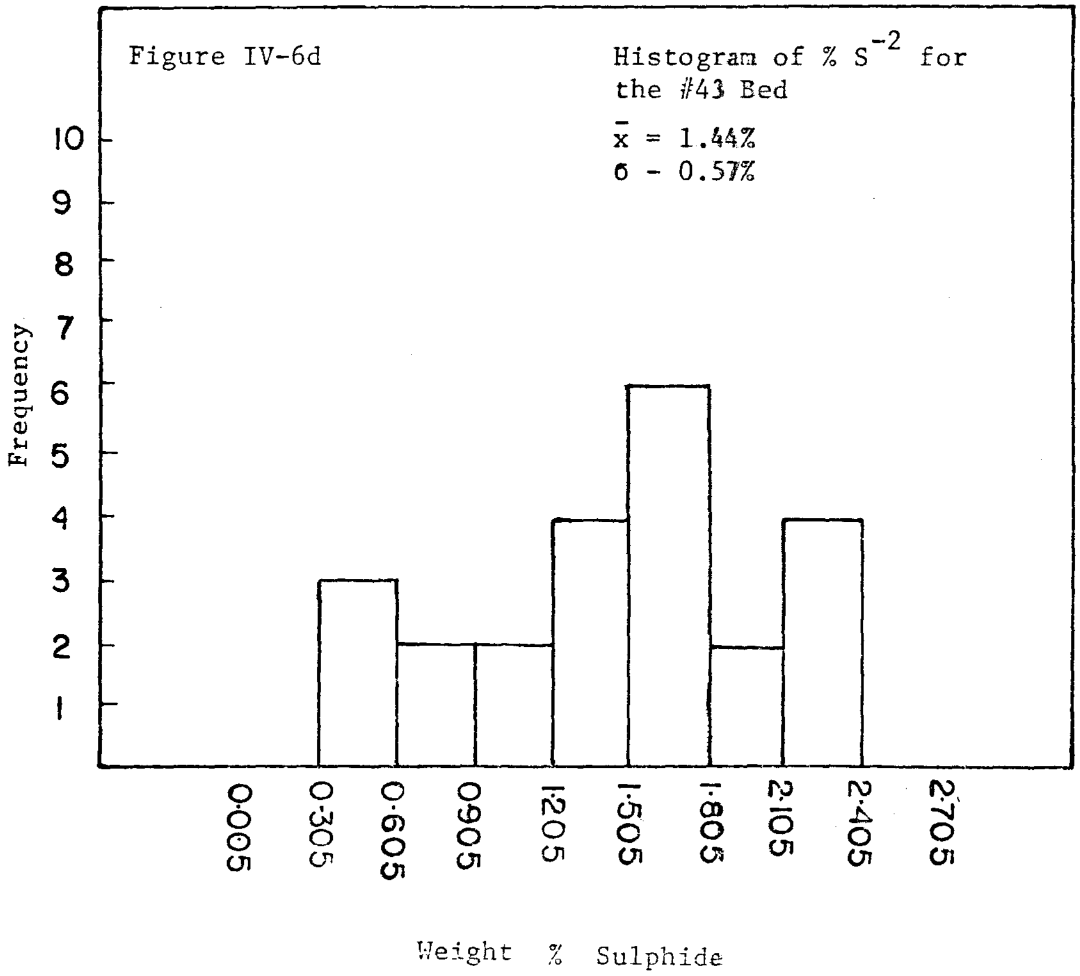


Figure IV-6d

Histogram of % S^{-2} for the #43 Bed

$\bar{x}$ = 1.44%

σ - 0.57%

Figure IV-6e

Histogram of % S^{-2} for the cupriferous zone adjacent to the transition zone

$\bar{x}$ = 1.11%
σ = 1.00%

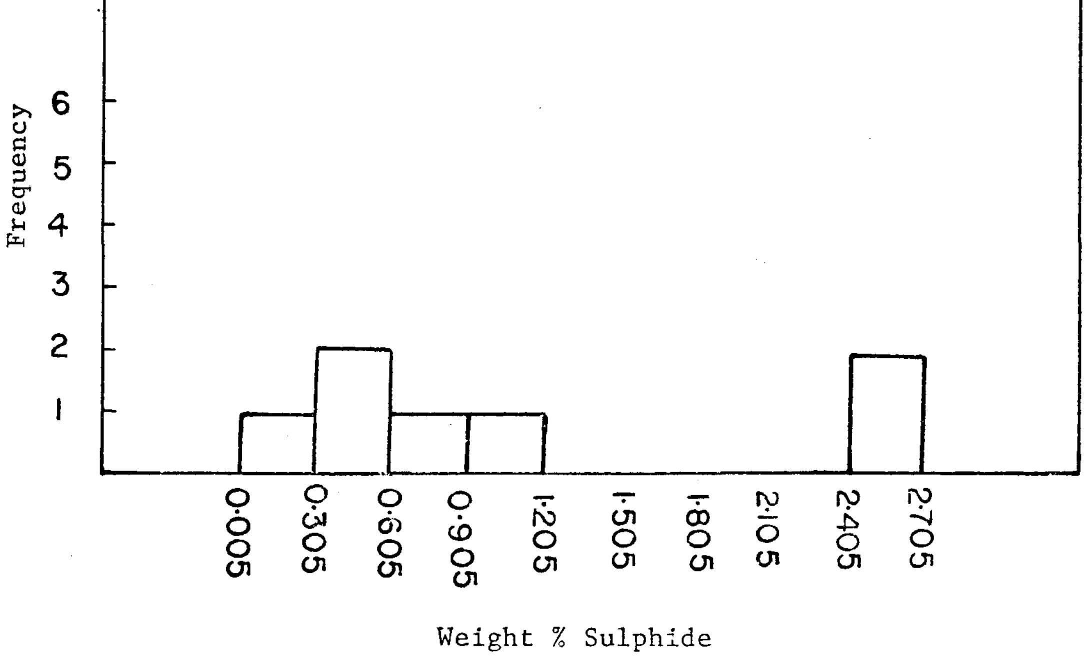
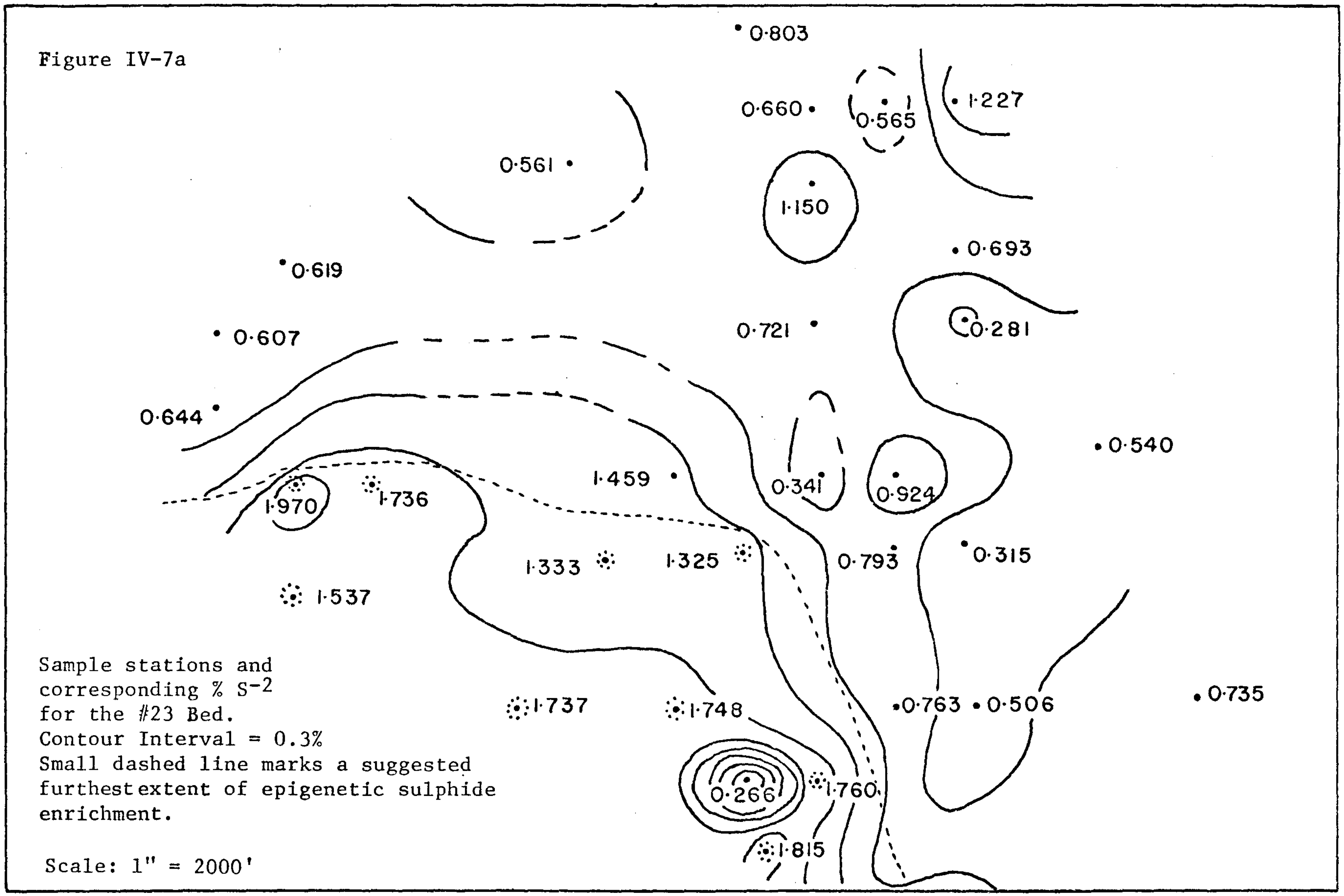


Figure IV-7a



Sample stations and corresponding % S^{-2} for the #23 Bed.
Contour Interval = 0.3%
Small dashed line marks a suggested furthest extent of epigenetic sulphide enrichment.

Scale: 1" = 2000'

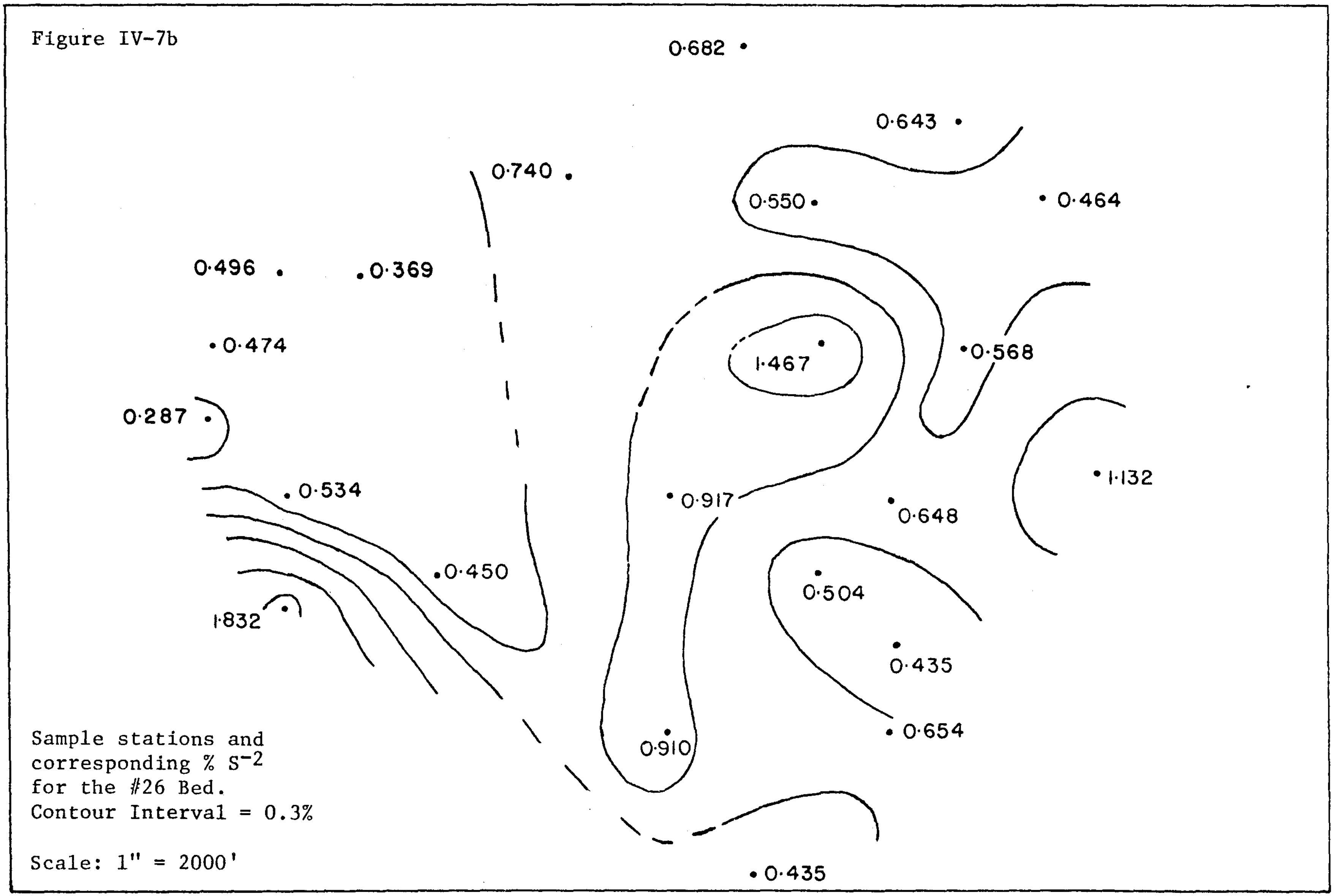
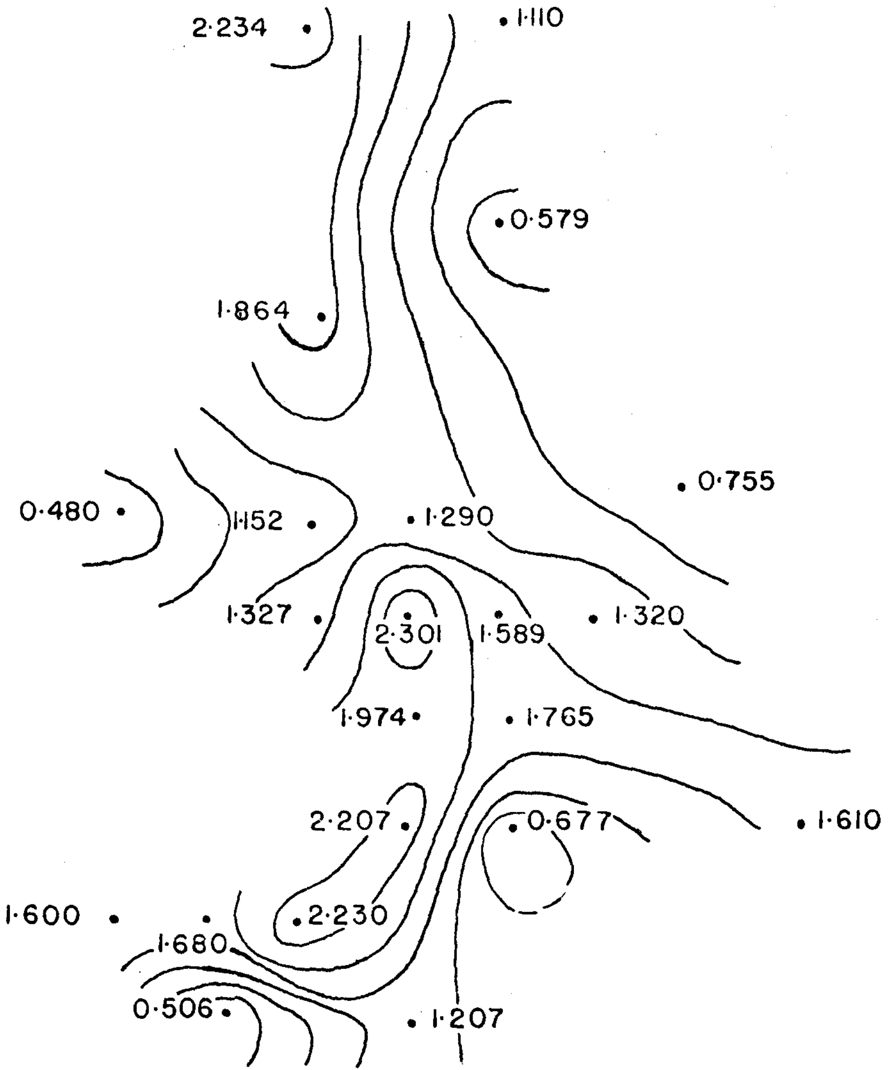


Figure IV-7b

Sample stations and corresponding % S^{-2} for the #26 Bed.
Contour Interval = 0.3%

Scale: 1" = 2000'

Figure IV-7c



Sample stations and
corresponding % S^{-2}
for the #43 Bed.
Contour Interval = 0.3%

Scale: 1" = 2000'

values. A similar strong areal correlation between these two variables cannot be demonstrated for the #23 and #26 beds. The relationship between sulphide per cents and δ values is more clearly seen in the linear plots of these variables in Figures IV-8a, b, c. Table IV-15 lists the linear correlation coefficient r, the Pearson-Product-Moment coefficient, and its level of significance for the plots in Figure IV-8.

TABLE IV-15: Values of "r" and its level of significance

	1	2	3	4
Stratigraphic Unit	r δS^{34} vs $\%S^{-2}$	N	$^{*}r_{0.95}$	$r_{0.99}$
Bed #23	-0.129	32	±0.297	±0.410
Bed #23 (corrected)	-0.610	23	±0.351	±0.483
Bed #26	+0.22	22	±0.361	±0.493
Bed #43	-.620	23	±0.351	±0.483

* Calculated from the equation $r_{0.95} = t_{0.95}/(t^{2}_{0.95} + N - 2)^{1/2}$ Dixon and Massey (1957).

A comparison of columns 1 and 4 of Table IV-15 shows clearly the significant negative linear correlation that exists between δS^{34} and sulphide per cent in the #43 bed. No significant linear correlation for these two variables occurs in the #23 and #26 beds. However, if in the #23 bed the nine data points 23-27E, 23-26G, 23-29AA, 23-25F, 23-27C, 23-30A, 23-29F, 23-30AA and 23-29D are eliminated from the linear correlation data (see Figure IV-8a) a very significant negative linear correlation exists between δS^{34} and sulphide per cent (see Table IV-15,

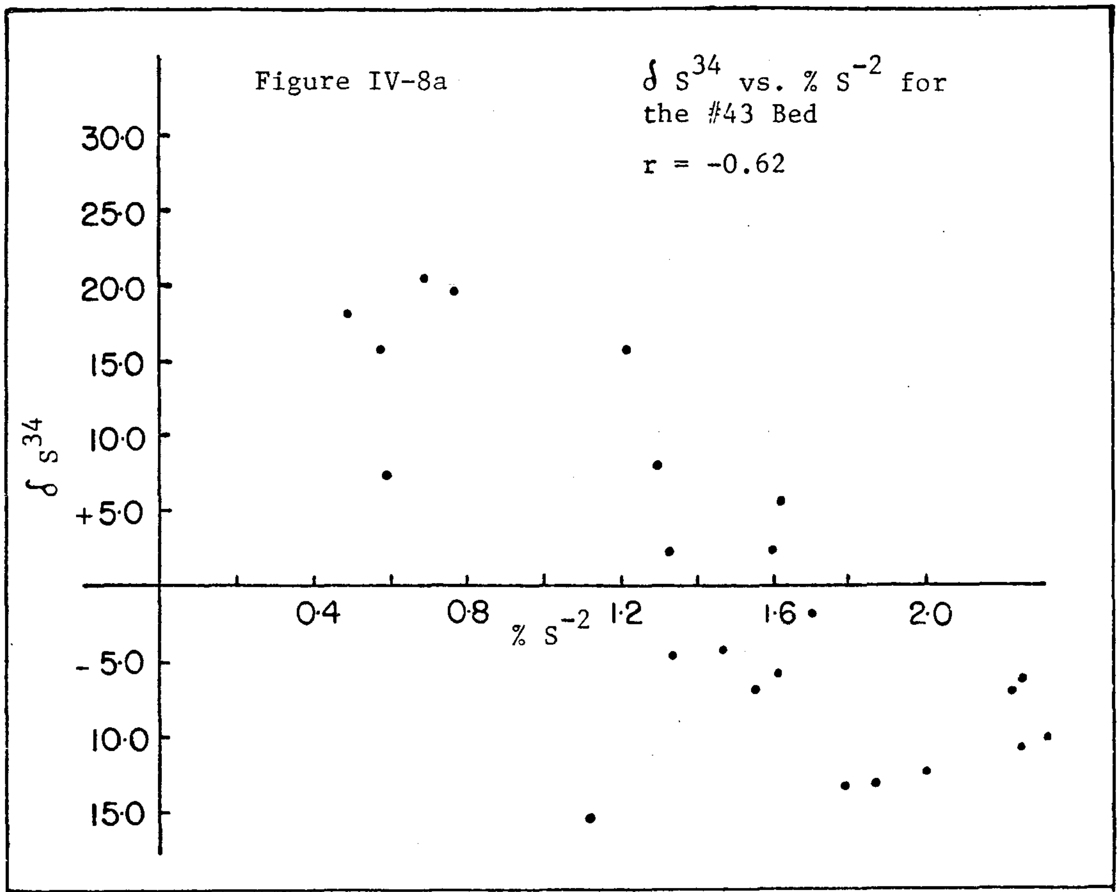


Figure IV-8a

δS^{34} vs. % S^{-2} for the #43 Bed

r = -0.62

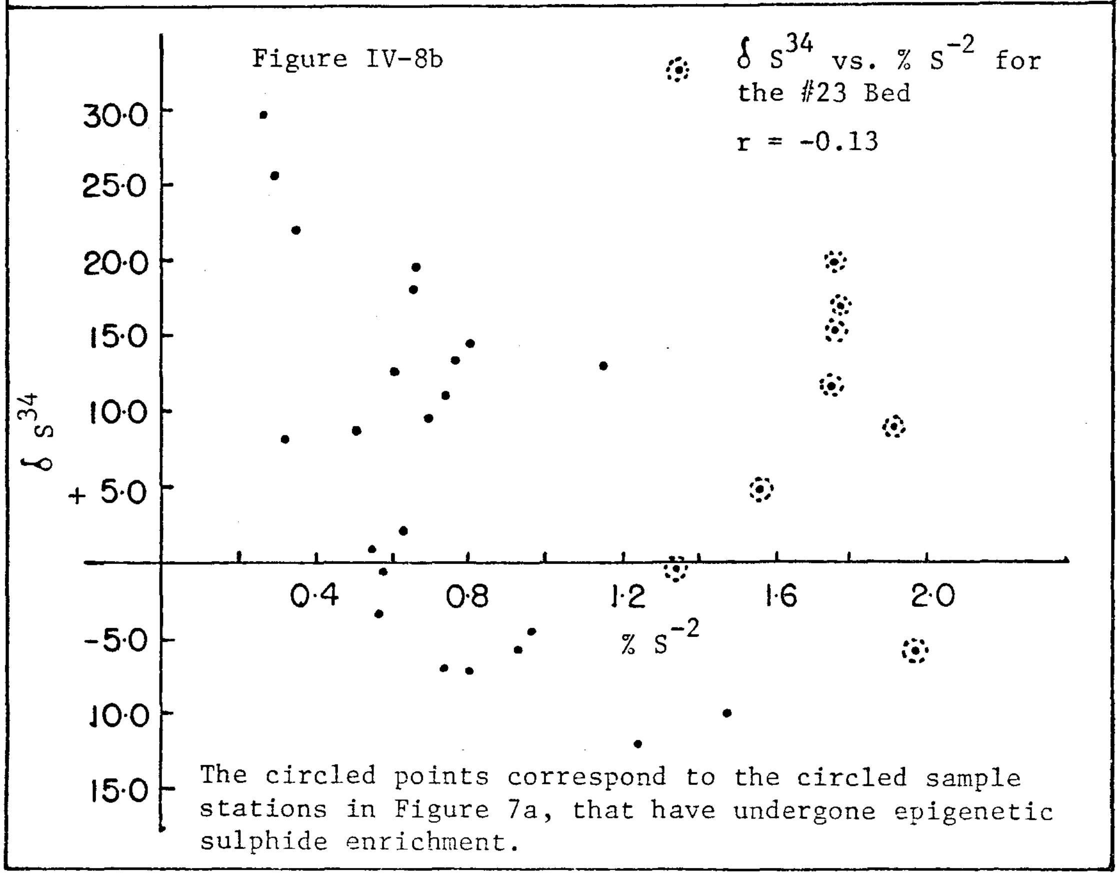


Figure IV-8b

δS^{34} vs. % S^{-2} for the #23 Bed

r = -0.13

The circled points correspond to the circled sample stations in Figure 7a, that have undergone epigenetic sulphide enrichment.

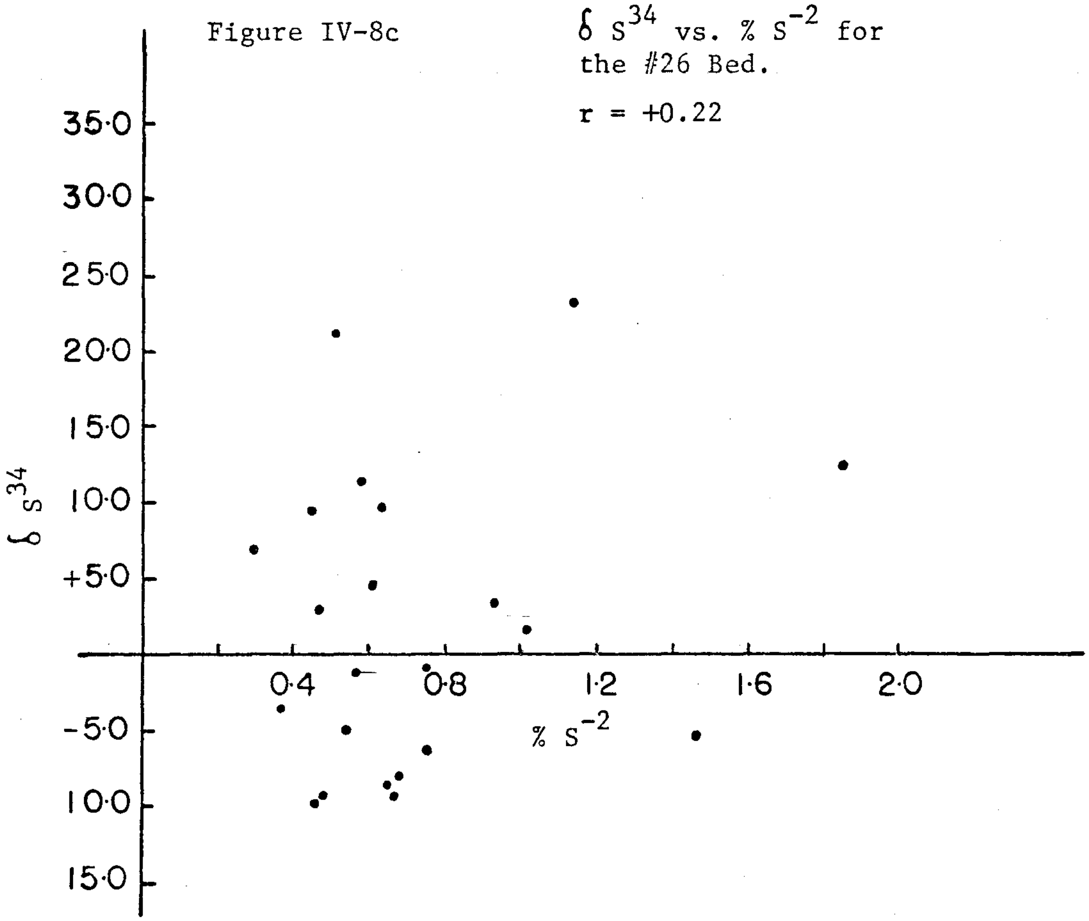


Figure IV-8c

δ S^{34} vs. % S^{-2} for the #26 Bed.

r = +0.22

bed #23 corrected). These 9 data points contain the highest sulphide per cents in the #23 bed and are closest to the White Pine fault (see Figure IV-7a). In view of these facts, it is tempting to suggest that this S.W. portion of the #23 bed has undergone sulphide enrichment from the White Pine fault. But, there has been no concomitant rehomogenization of the sulphur isotopes (see Figure IV-4a). It would be worthwhile to investigate in more detail the $\delta S^{34}-S^{-2}\%$ relationships not only for the #23 bed but also for the #26 and #43 beds in this portion of the mine.

(d) Paleoenvironment and Sulphide-δ Value Trends

The very significant negative correlation between δS^{34} and sulphide per cents for the #43 and corrected #23 beds is clearly related to the areal distribution of these variables in the former bed. But, this areal relationship is not so obvious in the latter unit. We may speculate that these relationships are the result of areal variations in the metabolic activity of the Precambrian sulphate reducers. In the laboratory Kemp and Thode (1968) found that a negative correlation between $\delta S^{34}_{\text{sulphide}}$ and rate of sulphate reduction was effected by the Hildenborough strain of Desulphovibrio desulphuricans when hydrogen was used as an electron donor. Kaplan and Rittenberg (1964) report this same correlation for similar laboratory experiments. This negative correlation was also found to occur when the bacteria metabolised at temperatures below their normal incubation value (Kemp and Thode, 1968). However, the most commonly found trend in the laboratory experiments is a positive correlation between δS^{34} and the rate of sulphate reduction. That is to say, an inverse relationship between the degree of fractionation and the rate of sulphate reduction (Harrison and Thode, 1958; Jones and Starkey, 1957; Kaplan and Rittenberg, 1964).

However, these laboratory experiments were completed over relatively short periods of time (a few weeks) and they involved one particular bacterial population living under controlled conditions. The samples from the #43 and #23 beds of the lower Nonesuch shale represent sulphides which probably accumulated over much longer and different periods of time, and which probably were formed by several distinct populations of sulphate reducers, subjected to uncertain environmental conditions. Also, it is not entirely evident that the rate of sulphate reduction in the paleoenvironment can be estimated by the percentage of sulphide contained within a rock sample. For these reasons, the comparisons between the relationships observed in the laboratory to those found in the field should be viewed critically.

The contoured δ value and sulphide percentage diagrams (Figures IV-9a, b, c, d) for the #23 and #43 beds can be compared to the lithological and copper-grade trends within these units as presented by White and Wright (1954). By superimposing Figure IV-9a over Figure IV-10a (from White and Wright, 1954, p. 699) a correlation between δ value trends and the lithology of the #23 bed can be shown. The N.E. - S.W. trending sand tongue, in the S.E. part of the White Pine Mine, is clearly flanked by the N.E. - S.W. ridge of high δ values. Similarly, by superimposing Figure IV-9b over 10a, a correlation between the shale facies and sandstone facies of Figure 10a with respectively the greatest and least sulphide percentages in Figure 9b is apparent. A similar correlation between the distribution of shale and sandstone, in the #23 bed, and copper grade was found by White and Wright (1954). There is not such a marked relationship, in the #43 bed, between lithological aspects (Figure IV-10b) and the contoured δ value and sulphide per cent

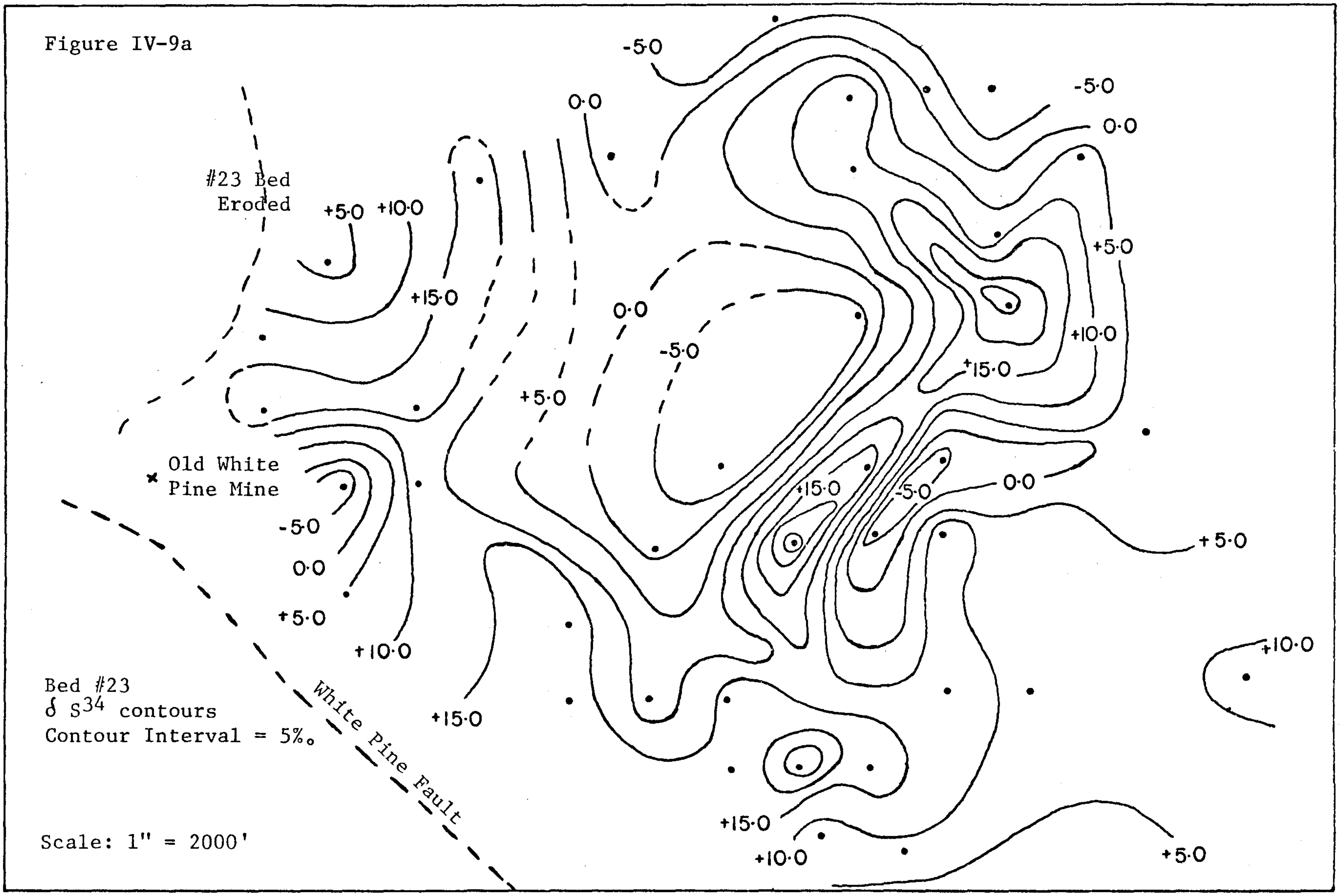


Figure IV-9a

Bed #23
$\delta\ S^{34}$ contours
Contour Interval = 5‰

Scale: 1" = 2000'

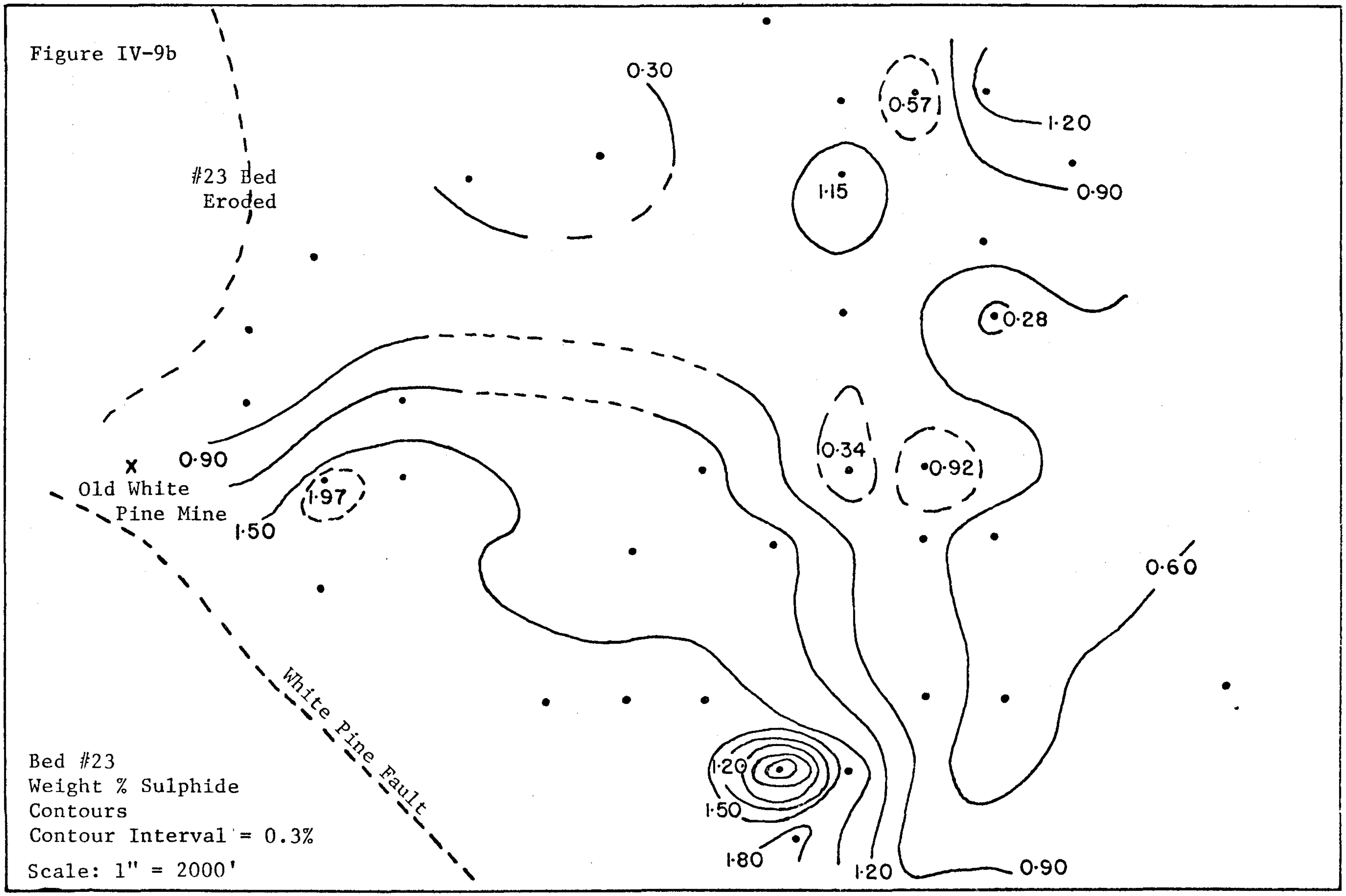


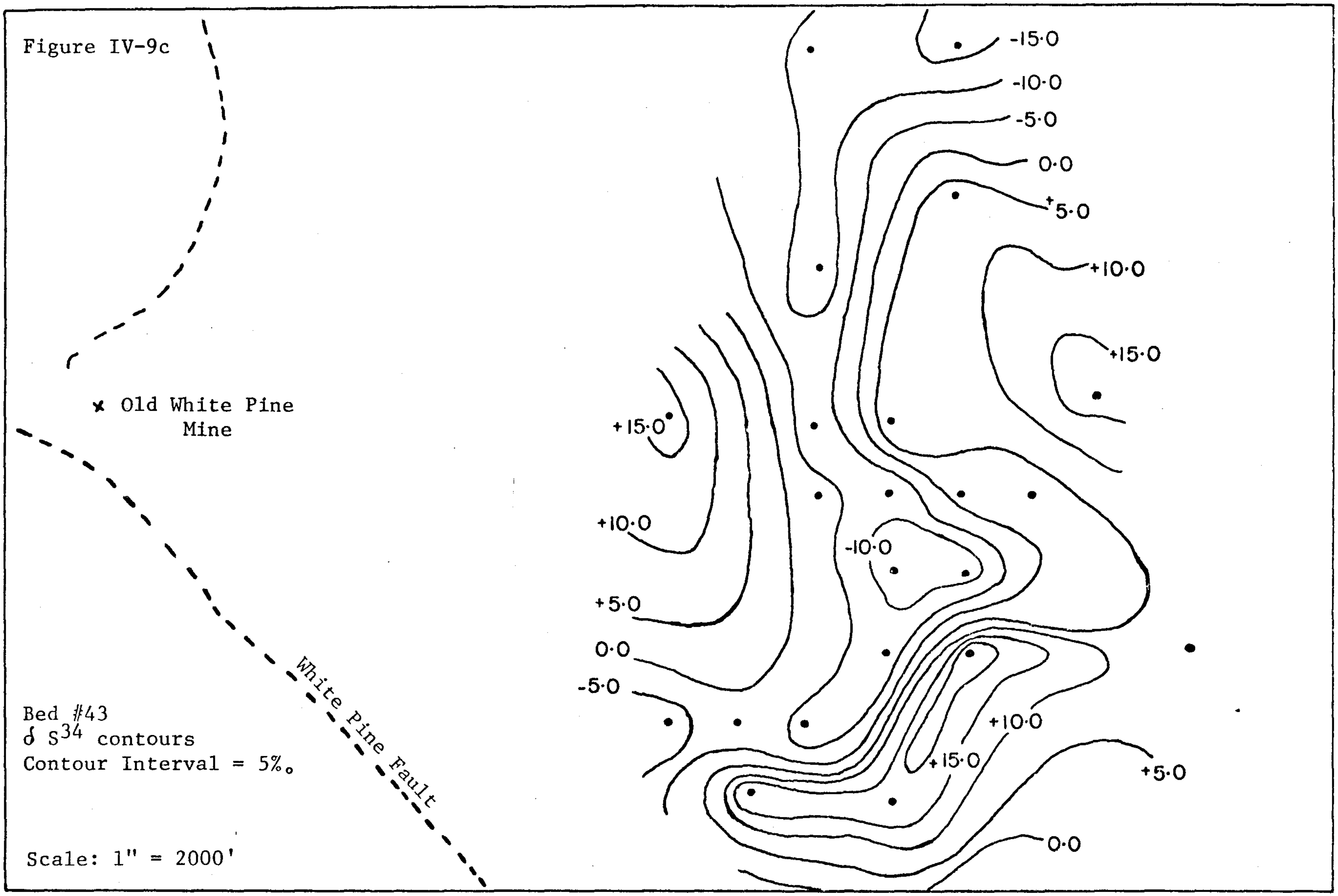
Figure IV-9b

Bed #23
Weight % Sulphide
Contours
Contour Interval = 0.3%
Scale: 1" = 2000'

Figure IV-10a : Lithofacies Map of Bed #23.

See Map Case at the Back .

Figure IV-9c



Bed #43
δ S^{34} contours
Contour Interval = 5‰

Scale: 1" = 2000'

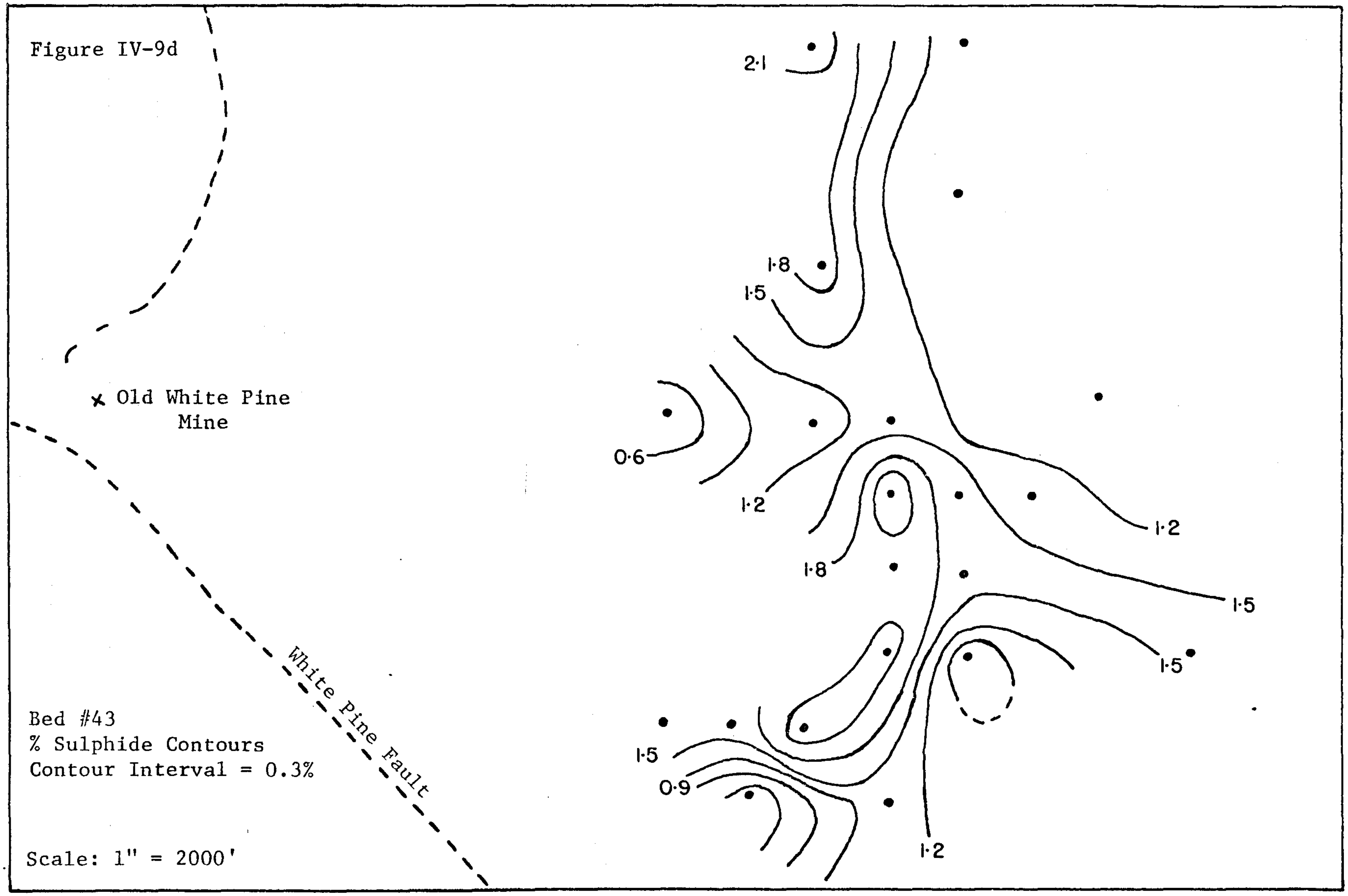


Figure IV-9d

Bed #43
% Sulphide Contours
Contour Interval = 0.3%

Scale: 1" = 2000'

Figure IV-10b : Lithofacies Map of Bed #43

See Map Case at the Back

Figure IV-10c : Lithofacies Map of Bed #30.

See Map Case at the Back.

diagrams (Figures IV-9c and 9d respectively). However, Figures 9c and 9d show closer affinities with the lithofacies map of the immediately underlying upper sandstone (Figure IV-10c). The N.E. trending sand tongue in the S.W. portion of the upper sandstone is flanked by a trough of low δ values and corresponding maximum sulphide percentages in the overlying #43 bed.

It must be emphasized at this time that these comparisons are subject to an error of scale incurred when the lithofacies diagrams in White and Wright (1954) were enlarged to 1" - 2000', the scale of the sulphide per cent and δ value diagrams. Also, the relationship of the ridges and troughs of sulphide per cents and δ values to the lithology may need revising or may in fact be negated when more detailed lithofacies maps based on thickness and sandstone:shale:siltstone ratios are made for the #10-#21 beds, #23 bed, #30 bed and #43 bed.

(e) Correlation between Sulphide and Total Carbon Contents

A comparison of the carbon and sulphide contents of the 3 ore horizons shows a significant positive correlation between these two variables for the #23 and #43 beds (see Figure IV-11a, b, c, and Table IV-16).

The association of sulphide and carbonaceous matter was studied in 40 thin sections and polished thin sections of the lower Nonesuch shale. Chalcocite was not uncommonly found to be in direct contact, perhaps replacing, individual red-brown fragments of organic matter. Chalcocite-free silicate bands, up to 20μ in thickness and made of 3μ to 10μ grains of quartz and feldspar enveloped by numerous dark to red-brown 1/2μ segmented threads of organic matter,* were very common in

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* For a further description, see Moore et al (1969).

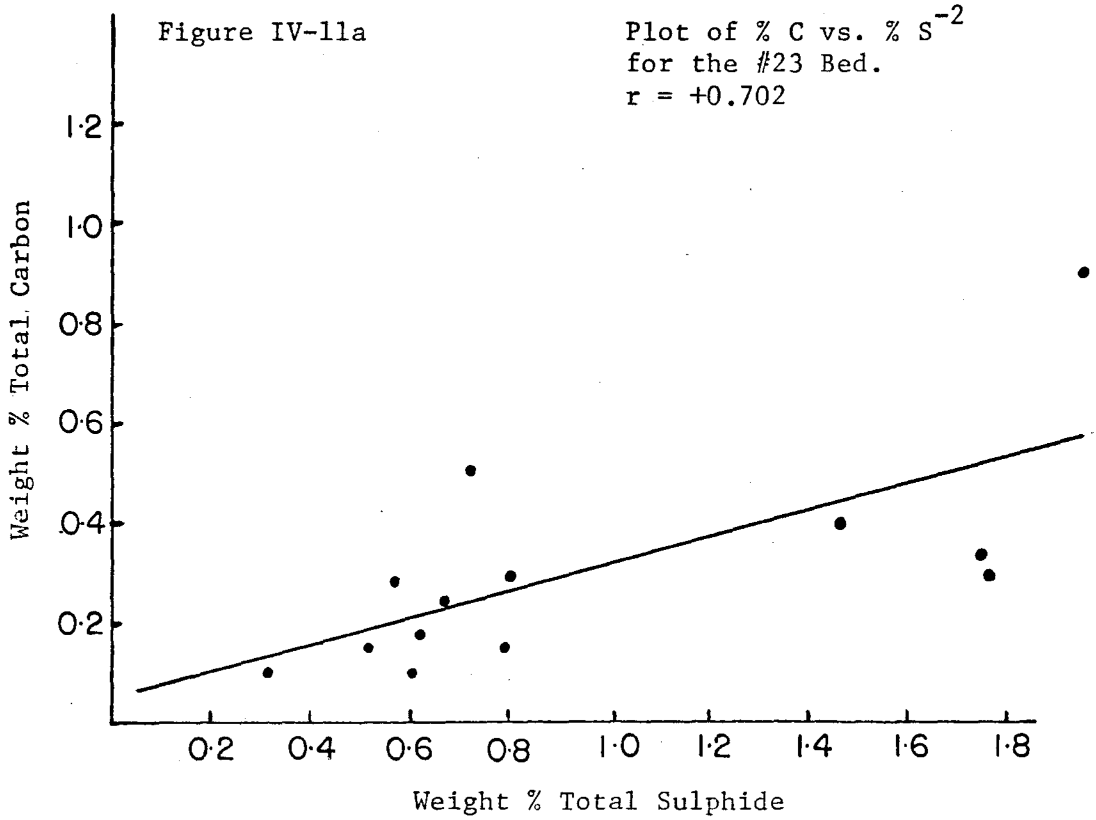


Figure IV-11a

Plot of % C vs. % S^{-2} for the #23 Bed. r = +0.702

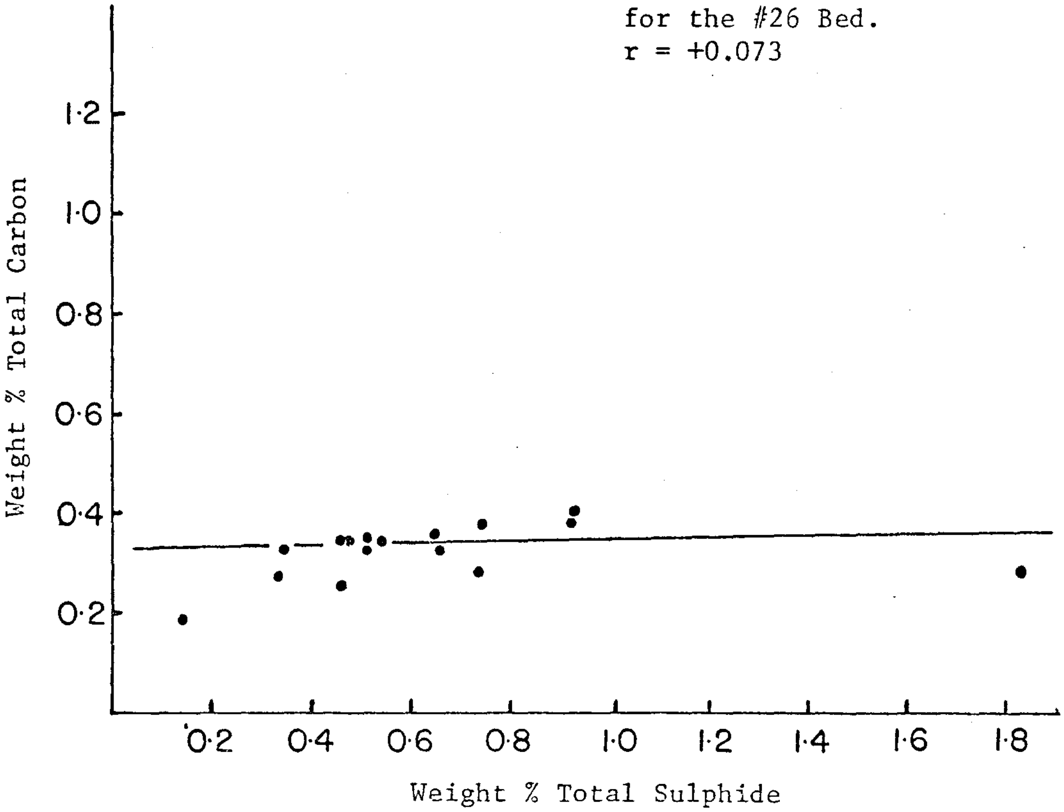


Figure IV-11b

Plot of % C vs. % S^{-2} for the #26 Bed. r = +0.073

Figure IV-11c

Plot of % C vs. % S^{-2}
for the #43 Bed
r = +0.609

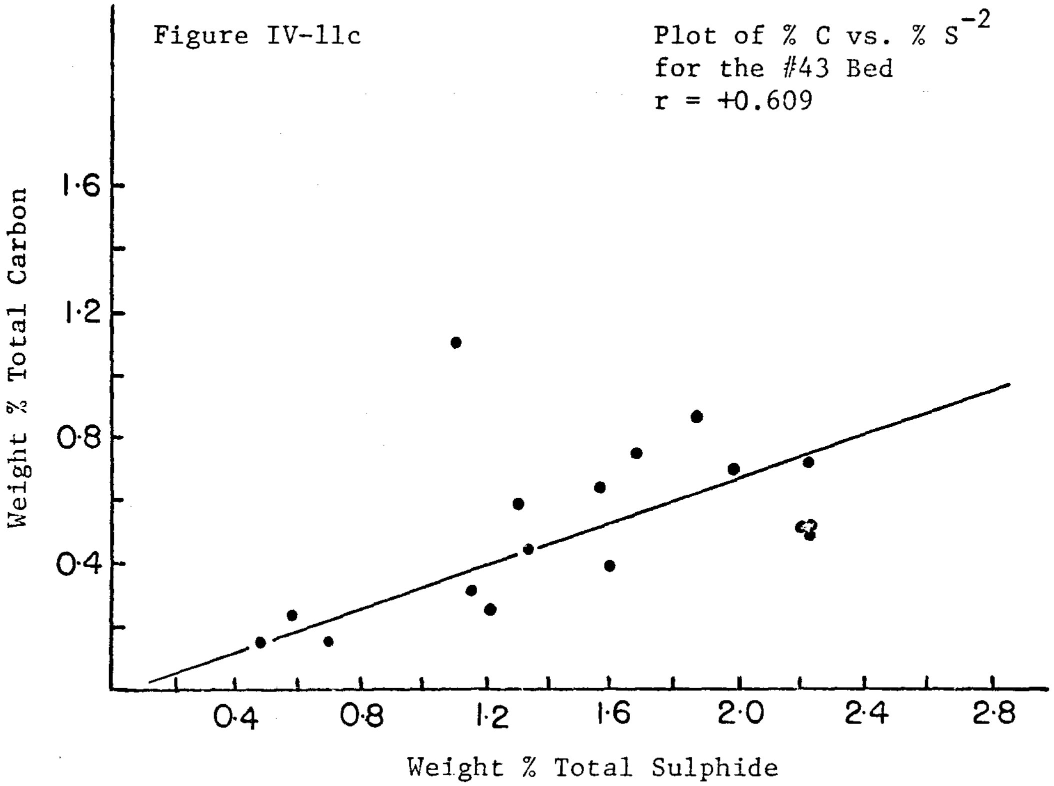
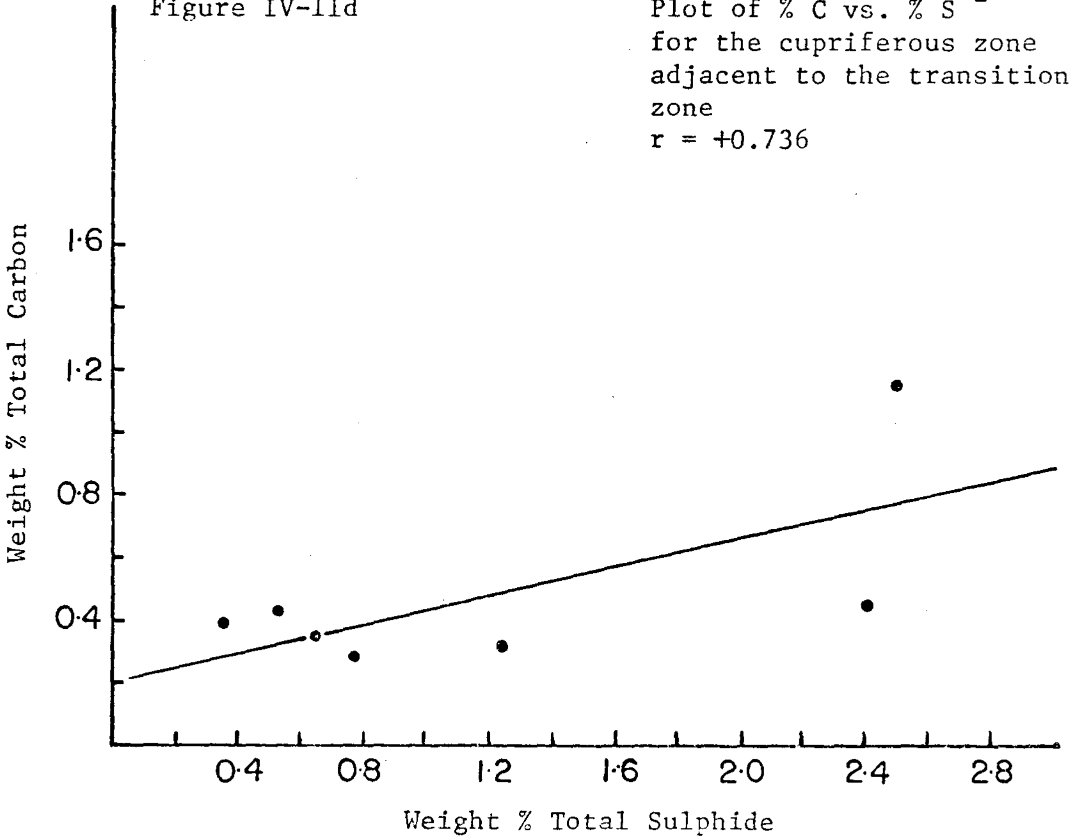


Figure IV-11d

Plot of % C vs. % S^{-2}
for the cupriferous zone
adjacent to the transition
zone
r = +0.736



all of the thin sections studied. One- to two-micron bands of concentrated organic matter were commonly threaded through laminae, 10 to 30μ thick, comprised of accumulations of less than 2μ grains. Therefore, in beds #23 and #43, the significant positive linear correlation between total carbon and weight per cent sulphide cannot be entirely attributed to the replacement of organic matter by chalcocite. The even concentration of carbon in the #26 bed (refer to Figure IV-5b and Table IV-13) and the consequent lack of linear correlation between total carbon and per cent sulphide (see Table IV-16 and Figure IV-11b) further emphasize that the relationship between these two variables is not due to replacement alone.

TABLE IV-16: Linear correlation data for weight % total carbon vs weight % sulphide

Stratigraphic Unit	Linear Correlation coefficient "r" for % C vs % S	$r_{0.975}$	Slope for linear regression of % C vs % S	Y intercept for lin. reg. of % C vs % S	N
Bed #23	+0.702	0.553	+0.262	+0.048	13
Bed #26	+0.073	0.482	+0.015	+0.328	17
Bed #43	+0.609	0.482	+0.346	-0.009	17
*Cpz/Tz	+0.736	0.754	+0.237	+0.197	7

* Cpz/Tz refers to the cupriferous zone adjacent to the transition zone.

The similarity between the slopes and y intercepts for the linear regression of % C on % S^{-2} for beds #23 and #43 (see Table IV-16) is interesting but of uncertain significance. Perhaps the positive correlation between per cent sulphide was a result of a nutrient-metabolic product balance in the Nonesuch shale paleoenvironment. That is, a greater amount of organic carbon is required to support a population of sulphate reducers producing a larger volume of sulphide.

(f) The Significance of the Relationship Between $\delta S^{34}_{\text{sulphide}}$ and Carbon Content

$\delta S^{34}_{\text{sulphide}}$ and the weight per cent Carbon show the same linear correlations for the #23, #26 and #43 beds as the plots of $\delta S^{34}_{\text{sulphide}}$ vs. weight per cent sulphide (see Figures 8a, 8b, and 8c). Consequently, the significance of the relationship between $\delta S^{34}_{\text{sulphide}}$ and the weight per cent Carbon will be discussed only briefly.

Assuming that carbon represents the nutrient of the sulphate-reducing bacteria, then more negative $\delta S^{34}_{\text{sulphide}}$ values should be associated with lower carbon contents, and more positive $\delta S^{34}_{\text{sulphide}}$ values (those approaching the value of $\delta S^{34}_{\text{sulphate}}$) should be associated with higher carbon contents. This is to be expected from the laboratory observations of the activity of Desulphovibrio desulphuricans (Jones and Starkey, 1957; Kemp and Thode, 1968). However, in the #43 bed of the lower Nonesuch shale, the reverse relationship occurs. That is, the more negative $\delta S^{34}_{\text{sulphide}}$ values occur with the higher carbon contents and the more positive $\delta S^{34}_{\text{sulphide}}$ values occur with lower carbon contents. This apparent contradiction to the laboratory results can be explained by considering the carbon nutrient content/size of bacterial population ratio, and the diluting effect of the sediment. Consider two simple cases: 1) a medium (sediment) containing a relatively high nutrient carbon content, and a very large bacterial population; 2) a medium (sediment) containing a relatively low nutrient carbon content, and a very small bacterial population. In the first case the nutrient carbon per sulphate reducer would be low and the bacteria would produce sulphide, with more negative $\delta S^{34}_{sulphide}$ values, at a low rate. However, since the bacterial population is large, the overall amount of sulphide in the sediment would be large. As a result, high carbon and sulphide contents in the sediments would be associated with more negative $\delta S^{34}_{sulphide}$ values. In the second case, the nutrient carbon per sulphate reducer would be high and the bacteria would produce sulphide at a rapid rate with more positive δS^{34} values. However, since the bacterial population is small, the overall sulphide content in the sediment would be low. Consequently, low carbon and low sulphide contents in the sediments would occur with more positive (approaching $\delta S^{34}_{sulphate}$) $\delta S^{34}_{sulphide}$ values.

Section 4: Boron

Boron was determined to 1) estimate the salinity of the lower Nonesuch paleoenvironment; and 2) to prove the presence or absence of the postulated ore solution (see White and Wright, 1966) by comparing boron contents in the sediments above and below the transition zone.

Boron was quantitatively determined for 24 samples from the lower Nonesuch shale using a 21 ft Jarrel Ash Co. grating spectograph. The method involved the analysis of the boron line 2496.48 A and the internal standard beryllium line 2494.58 in the second order. For a more detailed description of this method see Bugry (1964). The analyses, done in duplicate, are presented in appendix 5. As an estimate of error for this emission spectrographic method, the pooled standard deviation (Dixon and Massey, 1957, p. 109) for the 24 duplicate analyses was calculated to be +8.4 ppm.

The means of each six boron analyses for the #23, #26 and #43 beds and of the pyrite zone adjacent to the transition zone were compared statistically using a modified T test for small sample sizes (Dixon and Massey, 1957, p. 409). Table IV-17 lists the critical values for this test and the value of the significance test for the null hypothesis, $\mu_1 = \mu_2$. Data in this table show that the mean values of boron for the #43 and #23 beds differ significantly from each other, from the #26 bed and from the pyrite zone adjacent to the transition zone. Also the data show that the mean of the beds of the pyrite zone adjacent to the transition zone and the mean of the #26 bed are statistically the same. Since the boron mean value for the former unit is an average of analyses from three beds, which are the #47, #46 and #44 beds, the statistical statements concerning this mean are of uncertain value.

Boron is taken into and onto clay minerals contained within transported and deposited sediments in amounts generally increasing with increasing salinity of the surrounding aqueous medium. Consequently, marine shales and clays which are generally finer grained and have been exposed to a greater boron concentration than fresh water clays and shales will contain a larger amount of adsorbed boron (Shimp _et al_, 1969). According to Shimp _et al_ (1969) the best indicator of salinity is a combination of boron concentration and size of the less than 2μ grain size fraction of the sediment. These authors found that on the average, for a marine clay and fresh water clay containing the same percentage of the less than 2μ grain size fraction, there are 30 to 45 ppm. more boron in the former clay than in the latter. A more thorough discussion of boron as a predictor of salinity and paleosalinity can be found in: Potter _et al_ (1963), Tourtelot (1964), Shaw and Bugry (1966) and Cody (1970)

TABLE IV-17: Data for the modified T test of mean boron values

Compared Straiigraphic Units		Mean Boron Value		Range		Value of significance test	*Td_6, 0.95	N	
1	2	U_1	U_2	1	2			1	2
Bed #23	Bed #26	46.7ppm	66.3ppm	39	32	0.550	0.405	6	6
Bed #43	Bed #23	81.3ppm	46.7ppm	33	39	0.965	0.405	6	6
**Pyz/Tz	Bed #23	64.0ppm	46.7ppm	24	39	0.546	0.405	6	6
Bed #26	Pyz/Tz	66.3ppm	64.0ppm	32	24	0.082	0.405	6	6
Bed #43	Bed #26	81.3ppm	66.3ppm	33	32	0.462	0.405	6	6

* Refer to Table A-8c, Dixon and Massey (1957).

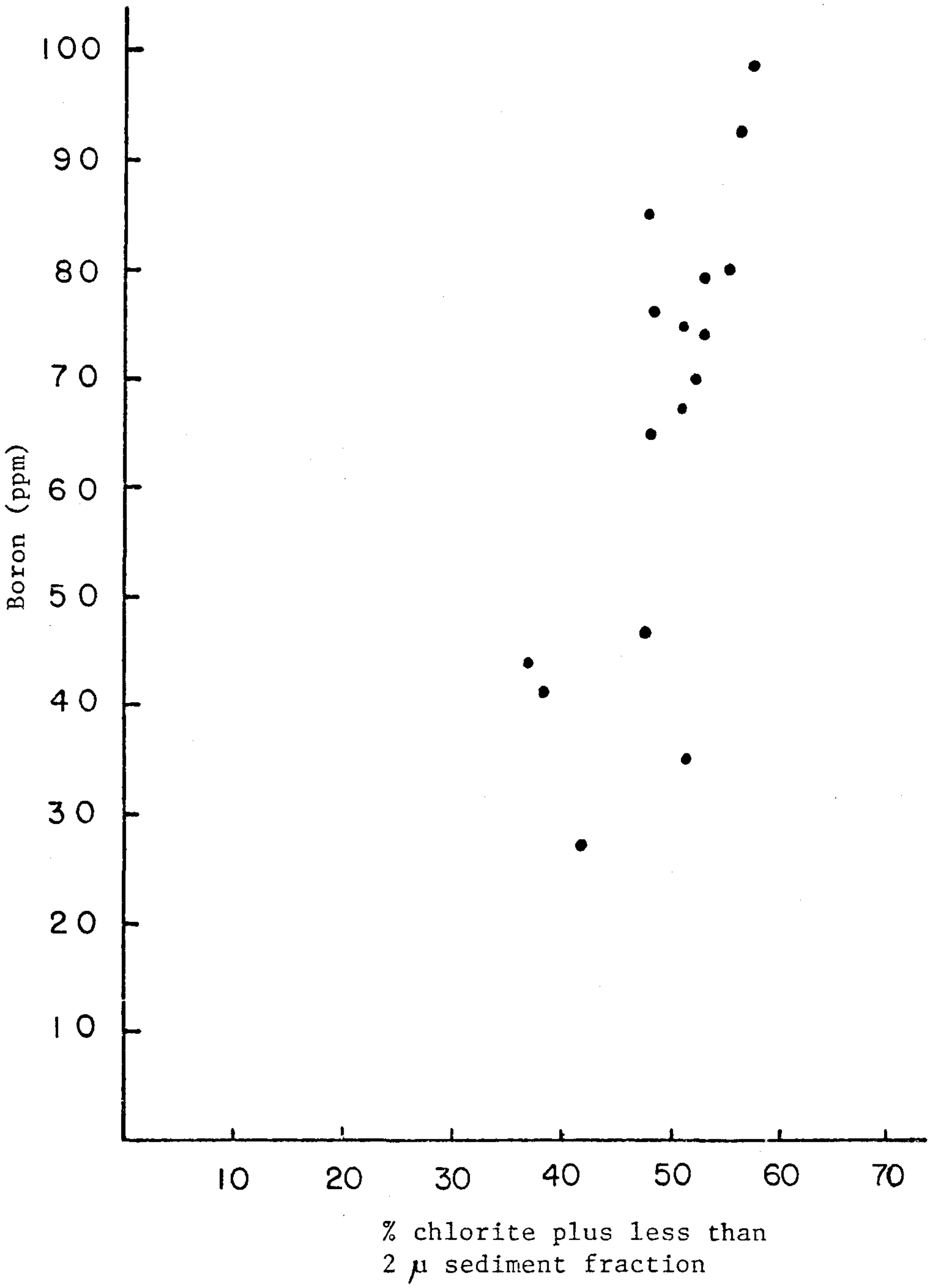
** Pyrite zone adjacent to the transition zone.

As an estimate of the less than 2μ sediment fraction of the lower Nonesuch shale, at the time of deposition, the modal abundance of chlorite plus the present less than 2μ grain size content was determined in 16 polished thin sections. Chlorite was included as part of the less than 2μ grain size fraction since this mineral is considered to be a diagenetic product of initial clay minerals (Jost, 1968; Whitehouse and McCarter, 1958). Five hundred points per thin section were counted at 1250x magnification using oil immersion and a calibrated ocular. The results are listed in appendix 5. To estimate an error for the modal analysis, recounts were done on 8 randomly chosen thin sections. The pooled standard deviation calculated from the duplicate analyses is ±1.2 modal per cent.

Figure IV-12 is a scatter diagram of ppm. boron vs. per cent less than 2u grain size plus chlorite content. A linear regression analysis determined the line of best fit for these 16 points to be $Y = 2.53\ x - 58.44$; where Y = ppm. boron and x = per cent chlorite plus less than 2μ grain size content. The linear correlation coefficient, r, is +0.72 which is highly significant at $r_{16,0.995}$. This equation differs from both of the regression lines $Y = 1.36\ x + 62.40$ and $Y = 1.06\ x + 34.96$ determined by Shimp <u>et al</u> (1969) for respectively marine and fresh water clays. This lack of similarity may be due in part to a contribution of chlorite formed by the alteration of ferromagnesian minerals such as pyroxenes and amphiboles in the Nonesuch sediments. These chlorites would have little genetic relationship to the clay minerals of the less than 2μ grain size fraction. Another possibility for this dissimilarity in regression lines is that the boron values from the lower Nonesuch shale have been taken from sediments representing marine, brackish, or

Figure IV-12

Scatter diagrams of ppm Boron
vs. Modal % chlorite plus the
less than 2 μ sediment fraction.



fresh-water environments. Therefore the Nonesuch boron regression line would be an average of the lines proposed by Shimp *et al* (1969). In view of this dissimilarity between the White Pine regression line and those determined by Shimp *et al* (1969), only a very general statement can be made regarding the boron results and the paleosalinity of the lower Nonesuch shale. If indeed the modal per cent of chlorite plus the present less than 2μ grain size fraction is representative of the less than 2μ fraction in the Nonesuch shale at the time of deposition, generally the lower Nonesuch sediments contain too little boron for a given clay content for these sediments to have been deposited in a marine environment. Judging from boron content alone (Shaw and Bugry, 1966) the Nonesuch sediments would be classed as brackish to fresh-water. The paleosalinity determined from the boron analyses is essentially in agreement with the deltaic-lagoonal paleoenvironment determined from the sedimentology and paleontology (White and Wright, 1954; Moore *et al*, 1969).

Boron determinations for the lower Nonesuch shale have been made by Reynolds (1965) and Vine and Tourtelot (1969). The former publication contains only one analysis taken from an unspecified stratigraphic position in the lower Nonesuch shale at the White Pine Mine. This author's analysis was done on the less than 2μ grain size fraction alone. Therefore his value of 137 ppm. boron cannot be readily compared to the results in this thesis. Vine and Tourtelot (1969) analysed 20 samples of the lower Nonesuch shale. Sixteen of these were taken from the striped #61 bed above the transition zone at the White Pine Mine. The authors found that 90% of their analyses fell between 100 and 20 ppm. boron. This range is in good agreement with the range, 27 ppm. to 97 ppm. boron, determined in this thesis. In Vine and Tourtelot's 1969 paper, boron has been classed, on a 2 factor vector diagram, in a detrital subgroup correlating well with titanium and sodium. These correlations are not contrary to the relationship between boron and the less than 2µ grain size content of the sediments.

If the transition zone is the furthest extent of a copper mineralized front, as proposed by White and Wright (1966) and by Brown (1965, 1968), then there should be some difference in boron values within the cupriferous and pyrite zones, provided that the ore fluid is either richer or poorer in boron than the Nonesuch "sea water". The similarity in the range of boron values within the cupriferous zone (this thesis) and pyrite zone (Vine and Tourtelot, 1969), at White Pine, does not support the ascending mineralization front hypothesis. However, it does not disprove this hypothesis. A more detailed geochemical study of the sediments within the cupriferous and pyrite zones, in which B, Na, Cl, Cu, Ca, K, and Sr are analysed in many samples, is required before the worth of the epigenetic mineralization hypothesis and consequently the origin of the transition zone can finally be evaluated.

Section 5: Chlorite in the Lower Nonesuch Shale

Modal X-ray analyses of the parting shale by Wiese (1960) and Moore et al (1969) show that chlorite forms on the average, 20-35 volume per cent of the rocks. From a thin section study, in this thesis, the chlorite shows a variety of habits, some of which are: laths, fibrous aggregates, radiating blade aggregates, tabular-prismatic blade aggregates and laths that are composed of several individual fibres. For many of the chlorites consisting of laths of fibres, it is difficult to determine if there are distinct fibres or if the chlorites exhibit only a well-developed cleavage. About four types of pleochroism were common: brown-green-brown; light green-clear (light yellow brown) -light green; blue green-clear-blue green; and green-brownish yellow-green. The interference colour of the chlorites ranged from anomalous blue to upper first order. No particular pleochroism was associated with a particular interference colour. All of the chlorites showed a wavy extinction. The lath shaped varieties were length slow. No interference figures could be detected in any of the chlorites studied due to their fine fibrous to bladed nature (fibres are generally less than 1µ in width) and due to the numerous inclusions in some varieties. Lath form chlorites were oriented parallel to the bedding or bowed around larger, 150µ to 50µ, silt-sized grains. The other fibrous and bladed forms were best developed in 50 to 100µ interstices of the silt fraction. It was not uncommon to observe the non-lath variety of chlorite replacing albitic plagioclase feldspar. The grain size of the lath chlorite variety is variable and can be as large as 100 x 15µ to 75 x 15µ to 45 x 30µ, and as small as 10 x 3µ to 20 x 1µ to 5 x 3µ.

Opaque and non opaque inclusions were most abundantly found in the lath variety. The size of inclusion varied to as large as 10 x 10µ to as small as 1/2 x 1/2u. Generally, they were less than 4 x 3µ. The shape of the inclusions varied as well, from rounded to subrounded to square to rod-like. Non-opaque,spherical and rod-like forms were consistent in size, respectively 1 to 1/2µ by 1 to 1/2 µ and 1 to 3 x 1/2µ. The colour of these two varieties was generally bright to light red-brown. Some of the larger opaque inclusions, 3µ and over, took a polish and were identified as being most probably chalcocite. These inclusions with little exception were oriented parallel to the long axis of the chlorite laths and blades. Opaque ore inclusions within the lath forms resembled, in shape and size, the red to dark brown non-opaque inclusions contained in the same chlorite. The chlorites do not appear to be replaced by the contained ore grains.

Carpenter (1963) identified the chlorite in one particular vein in the lower Nonesuch shale as type Ib (Bailey and Brown, 1962). According to Bailey and Brown (1962) this polytype of chlorite is characteristically diagenetic and typical of the variety found in the Lake Superior iron formations. It is important to identify the types of chlorites in the lower Nonesuch shale in order to establish genetic differences or similarities between the lath shaped varieties, which on the whole are more frequently mineralized with sulphides, and the other forms.

What proportion of the chlorites in the lower Nonesuch shale were authigenic as opposed to clastic was not determined in this thesis. Part of the authigenic variety may have been derived from the alteration of ferro-magnesian minerals such as amphiboles and pyroxenes within the sediments. However, most of the authigenic chlorite was probably formed by the interaction of clay minerals with the Nonesuch sea water. Such a diagenetic origin for chlorites has been proposed by Whitehouse and McCarter (1958) and has been very adequately discussed for the Nonesuch environment by Jost (1968).

CHAPTER V

A COMPARISON OF THE δ VALUE DISTRIBUTION OF THE LOWER NONESUCH SHALE AT THE WHITE PINE MINE TO DISTRIBUTIONS IN OTHER DEPOSITS

The wide spread in $\delta S^{34}_{\text{sulphide}}$ for the cupriferous zone at the White Pine Mine can be compared to the variations in δ values for other stratiform sulphide deposits such as Mount Isa (Stanton and Rafter, 1966), Mufulira (Dechow and Jensen, 1965), Gas Hills district (Cheney, 1966) and the Kupferschiefer (Marowsky, 1969) (see Table V-1, and Figure V-1).

TABLE V-1: Comparison of δS^{34} values for stratiform and magmatic hydrothermal sulphide deposits

Stratiform Sulphide Deposits	Mean $\delta S^{34}_{\text{sulphide}}$	Range	Standard Deviation	N	Age
White Pine Mine Lower Nonesuch Shale	+3.5‰	48.3‰	11.7‰	94	Late Keweenawan
Mount Isa	+10.7‰	7.2‰	2.3‰	14	Lower Proterozoic
Mufulira N. Rhodesia	+0.9‰	21.4‰	4.3‰	52	Late Precambrian
Gas Hills District Syngenetic Pyrite	+3.7‰	36.0‰	10.6‰	30	Lower Eocene
Kupferschiefer	-29.9‰	40.0‰	8.3‰	93	Permian
Magmatic Sulphide Deposits					
Bingham, Utah	-0.6‰	10.0‰	1.5‰	40	
O'okiep	+0.8‰	10.0‰	1.0‰	33	

Figure V-1a

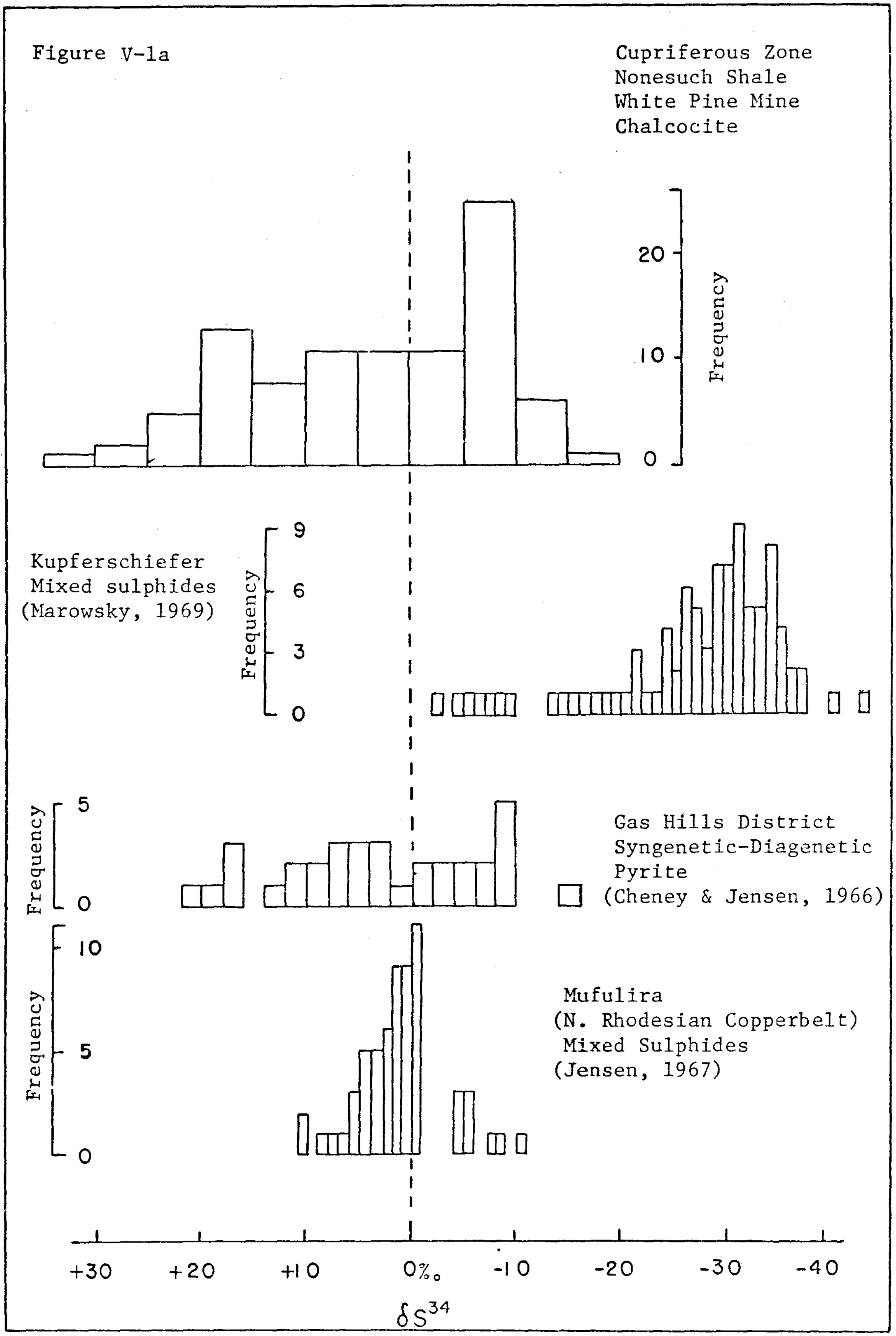
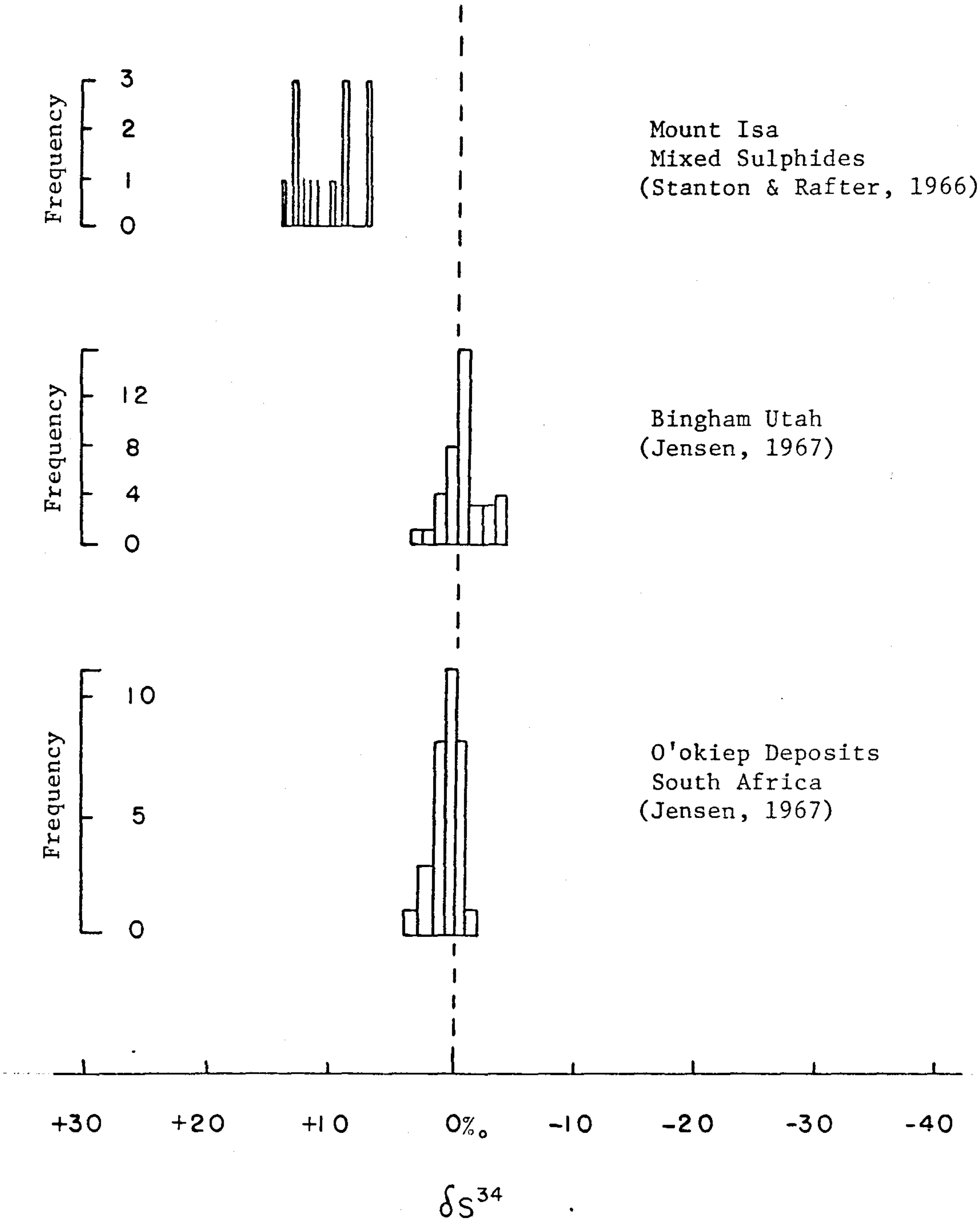

Cupriferous Zone
Nonesuch Shale
White Pine Mine
Chalcocite
20
10
0
Frequency
Kupferschiefer
Mixed sulphides
(Marowsky, 1969)
Frequency
9
6
3
0
Frequency
5
0
Gas Hills District
Syngenetic-Diagenetic
Pyrite
(Cheney & Jensen, 1966)
Frequency
10
5
0
Mufulira
(N. Rhodesian Copperbelt)
Mixed Sulphides
(Jensen, 1967)
+30
+20
+10
0‰
-10
-20
-30
-40
δS34

Figure V-1b


Frequency
3
2
1
0
Mount Isa
Mixed Sulphides
(Stanton & Rafter, 1966)
Frequency
12
8
4
0
Bingham Utah
(Jensen, 1967)
Frequency
10
5
0
O'okiep Deposits
South Africa
(Jensen, 1967)
+30
+20
+10
0‰
-10
-20
-30
-40
δS34

The range and standard deviation for $\delta S^{34}_{\text{sulphide}}$ in the cupriferous zone of the lower Nonesuch shale agrees well with these values for the biogenic sulphides of the Gas Hills district and the Kupferschiefer. But the mean $\delta S^{34}_{\text{sulphide}}$ value for the lower Nonesuch shale is very different from the mean $\delta S^{34}_{\text{sulphide}}$ value for the Kupferschiefer.* A possible explanation for this is that the mean $\delta S^{34}_{\text{sulphate}}$ values for the two geological times (Precambrian and Permian) of the deposits were different (Thode and Monster, 1965). Mount Isa, and Mufulira (Zambian Copperbelt) are stratiform ore deposits, but their $\delta S^{34}_{\text{sulphide}}$ ranges and standard deviations (see Table V-1) are much less than would be expected if their sulphides were biogenic. However, their mean $\delta S^{34}_{\text{sulphide}}$ values and standard deviations are not typically magmatic (see Table V-1).** The degree of structural control which the sulphides show in the Mount Isa deposit (Edwards, 1953) and the extent of metamorphism which the Mufulira deposit has experienced (Mendelsohn, 1961) makes it difficult to class these two deposits with the little deformed, virtually unmetamorphosed, biogenic Nonesuch sulphide deposit.

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* The mean, standard deviation and range for the Kupferschiefer was calculated from the data in Figure 2 of Marowsky (1969).

** This problem is dealt with more fully by Dechow and Jensen (1965) and Stanton and Rafter (1966).

CONCLUSIONS

1) The range and standard deviation (σ) of $\delta S^{34}_{\text{sulphide}}$ from 94 specimens of White Pine ore indicate a biogenic origin for the sulphide in this deposit.

2) The mean and standard deviation of $\delta S^{34}_{\text{sulphide}}$ for the White Pine Mine as a whole, for the #23, #26 and #43 beds and for the cupriferous zone adjacent to the transition zone are respectively: $+3.5 \pm 11.7‰$, $+8.6 \pm 11.1‰$, $+1.3 \pm 9.2‰$, $-0.24 \pm 11.6‰$ and $-4.4 \pm 12.9‰$.

3) The mean $\delta S^{34}_{\text{sulphide}}$ value of the #23 bed is statistically more positive than the means of the overlying units analysed. However, the validity of the apparent trend for overlying units to become increasingly more negative is statistically uncertain.

4) Assuming a common bacterial fractionation effect interval of 0 to 25 per mil for the Precambrian sulphate reducers, the $\delta S^{34}_{\text{sulphate}}$ of the basal Nonesuch paleoenvironment can be estimated as $+15 \pm 2‰$.

5) A correspondence exists between the orientation and position of contour trends in the diagrams showing the areal distribution of $\delta S^{34}_{\text{sulphide}}$ and % S^{-2} in the #23 and #43 beds, and trends in the lithofacies, isopach and copper grade maps for respectively the #23 and #30 units.

6) There is a significant negative correlation between $\delta S^{34}_{\text{sulphide}}$ and the % S^{-2} in the #43 unit. This relationship is clearly associated with the areal distribution of these variables within this unit. A similar

negative correlation exists between $\delta S^{34}_{\text{sulphide}}$ and % S^{-2} in the #23 unit, when it was corrected for the influence of a sulphide enrichment from the White Pine fault. However, there is no clear areal relationship between these parameters within this bed.

7) Contoured areal sulphide distributions in combination with a plot of $\delta S^{34}_{\text{sulphide}}$ vs. % S^{-2} for the #23 unit define an epigenetic component of the sulphide mineralization which is related to the White Pine fault.

8) The lack of significant linear correlation between weight per cent carbon and weight per cent sulphide in the #26 bed, is in contrast to the significant linear correlations between these two variables in the #23 and #43 beds. This contrast may be related to the differences in lithology of the units. The #23 and #43 units are finely interlaminated dark grey siltstones and shales, while the #26 bed is a massive dark grey siltstone.

9) The variables % C , % S^{-2}, and $\delta S^{34}_{\text{sulphide}}$ are not interrelated in the #26 bed as they are in the #43 and #23 units. This may be the result of a diagenetic redistribution of carbon and sulphide contents within the #26 unit.

10) The positive linear correlation between % C and % S^{-2} in the #43 unit, implies a negative linear correlation between % C and $\delta S^{34}_{\text{sulphide}}$ in this bed. Laboratory experiments (Kemp and Thode, 1968) indicate a positive correlation between $\delta S^{34}_{\text{sulphide}}$ and the rate of H_2S production, and $\delta S^{34}_{\text{sulphide}}$ and the amount of nutrient available to the sulphate-reducing bacteria. However, negative correlations between $\delta S^{34}_{\text{sulphide}}$ vs. % S^{-2} and between $\delta S^{34}_{\text{sulphide}}$ vs. % C are observed in the lower Nonesuch shale. This

apparent contradiction between the field results and the empirical relationships can be resolved by considering the carbon nutrient/size of bacterial population ratio, and the diluting effect of the sediments.

11) Boron analyses of the cupriferous zone samples suggest a brackish to fresh water paleoenvironment for the basal Nonesuch shale. The similarity in the range of boron values within the cupriferous and pyrite zones does not support the contention that the cupriferous zone has been mineralized by a copper-rich brine, assuming that there is some difference between the boron contents of the ore fluid and the Nonesuch "sea water".

12) On the basis of the range and standard deviation (6) for $\delta S^{34}_{\text{sulphide}}$, as well as the geologic association, the White Pine deposit shows analogues to the Kupferschiefer. However, the mean $\delta S^{34}_{\text{sulphide}}$ for the two deposits are considerably different due to differing $\delta S^{34}_{\text{sulphate}}$ values for the sea waters of the two geological time periods (see Thode and Monster, 1965).

13) Jost's (1968) mineralization hypothesis can be modified in the following way. Copper within the clay minerals, at the time of mineralization of the basal Nonesuch shale, was exchanged for cations such as Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+} present in the porewater of the sediments. The expelled copper was probably complexed with chloride to form the complex $CuCl_3^{2-}$.* This complex may have then moved down a copper ion concentration

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* If the abundance of copper (I) complexes are determined for various concentrations of the chloride ion (Butler, 1964), the $CuCl_3^{-2}$ ion is the most abundant complex (80%) assuming an activity of 0.36 moles/litre for the chloride ion in sea water (Garrels and Christ, 1965). This may not be a good assumption for the activity of the chloride ion in the sea water during the late Precambrian.

gradient (Berner, 1969) to the portions of the sediment where biological activity produced the sulphide ion. Here the copper complex was precipitated as a sulphide. In this model the sulphide ion is limiting and its absence enhances the probability of the formation of native copper and native silver. Eh-pH, copper complex and sulphide concentrations, the Cu/Fe ratio and the free energy of the reaction of the $CuCl_3^{-2}$ complex with either HS^- or H_2S are important parameters in determining the abundance and type of copper mineralization.

The original upper and lower boundaries of the cupriferous zone have been confused by later generally weak copper mineralizations (Jost, 1968; Hamilton, 1967) probably the result of respectively ascending and descending copper enriched porewaters expelled from the cupriferous zone during the compaction of the sedimentary pile. This point of view differs partly from Jost's which considers the third mineralization sequence, which confused the position of the original upper boundary, to have been formed by a later slight descending cementive copper mineralization. This, however, is contrary to his conclusion that the descending copper mineralization sequence in the #10 bed (lower sandstone) is an indication of descending copper solutions from the overlying Nonesuch shale.

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APPENDIX 1 Reagents

Reducing Solution

473 ml HI (S.G. = 1.7)

772 ml concentrated HCl

232 ml H_3PO_2 (50%)

Boil for 45 minutes

Cadmium Acetate Solution

62.5 gms Cadmium acetate

500 ml acetic acid (17N)

2000 ml distilled water

Silver Nitrate Solution (0.5N)

170 gms $AgNO_3$

2000 ml triply distilled water

Store in a coloured glass bottle

APPENDIX II Ungrouped $\delta S^{34}_{sulphide}$

Bed #	Sample #	δS^{34}‰
23	27E	+15.37, +15.09
	26G	+16.77, +16.76
	27H	+13.00
	29AA	+5.00, +5.72
	25F	+8.79, +9.17
	27C	+20.00, +19.76
	26F	+29.06, +29.26
	34G	+12.77, +12.97
	33I	+9.20
	30A	+11.52
	29F	+32.46, +31.06
	32I	+25.16
	27L	+10.85
	31K	+1.10
	30G	+22.02
	34J	+5.41
	29H	+14.12
	27I	+8.42
	32BB	+12.49
	31BB	+17.82
	33AA	+2.38
	35G	+19.32
	29I	+7.99
	26E	+15.40
	31A	+16.81
	27D	+9.84
	28C	+19.66
	34B	+16.76
	30AA	-5.38, -5.60
	30E	-9.88, -10.11
	23H	-4.29
	35H	-1.43
	29D	-0.66, -0.27
	35I	-12.06, -12.54
	30H	-5.51
	34D	-3.14
	36F	-7.11
	32G	-6.64
	29G	-8.00

APPENDIX II cont'd

Bed #	Sample #	δS^{34}‰
26	31BB	+0.68
	28H	+9.14
	31K	+23.20
	35I	+9.18
	29G	+4.06
	27E	+1.63, +1.81
	29AA	+12.48, +12.81
	34J	+2.93
	33AA	+21.31
	32I	+11.46
	30E	+3.42, +3.76
	27L	+0.4
	32G	-5.18, -5.73
	36F	-8.04
	32BB	-9.08, -9.04
	29B	-9.67, -9.52
	27H	-8.13
	25F	-1.47, -1.36
	30H	-8.98
	34G	-1.84
	30AA	-4.97
	33A	-3.37
	34D	-6.83
	32F	-0.72
43	31K	+19.33
	30H	+7.82, +7.61
	29J	+2.17, +1.83
	33I	+7.39
	29I	+2.51, +2.67
	25F	+15.41
	27L	+5.75, +6.07
	27I	+20.22
	30E	+17.90
	25H	+17.90
	27H	-6.86, -6.71
	23H	-6.61
	29G	-4.80
	35G	-10.22, -10.09
	28H	-12.13, -12.22
	32G	-12.64, -11.99

APPENDIX II cont'd

Bed #	Sample #	δS^{34}‰
43	28I	-12.71, -12.44
	26G	-6.23, -6.28
	26F	-1.86, -1.63
	26E	-5.90, -6.14
	29H	-9.81, -9.50
	35I	-15.83
	30G	-7.69
	36F	-8.94

Cupriferous Zone Adjacent to the Transition Zone

#46	34-1/4 C 1/4	-7.15
lower #44	27L	-10.75
#46	30H	-9.10
upper #43	27L	-9.47, -9.48
#46	33 1/4 f 1/8	+24.60
upper #46	29-1/4 J	-9.77
lower #46	34 1/2-I 1/8	-9.19

APPENDIX IIb Park City Pyrite $\delta S^{34}_{\text{sulphide-PCP}}$ (uncorrected)

+0.13
+0.13
+0.02
+0.12
+0.15
+0.07
-0.93
0.00
-0.55
-0.18
-0.71
-0.29
-0.47
-0.51
-0.86
-0.15
-0.77
-0.81
-0.60
-0.75
-0.84
-0.71
-0.56
-0.05
-0.85
-0.21
-0.19
-0.93
-0.73

-0.67
-0.56
-0.57
-0.18
-0.81
-0.35
-0.54
-0.80
-0.51
-0.44
-0.44
-0.11
-0.24
-0.44
0.00
-0.14
-0.26
-0.37
-0.31
-0.04
-0.11
-0.47
-0.18
-0.42
-0.33
-0.33
-0.15
-0.07
-0.15

-0.37
-0.04
-0.25
-0.55
-0.48
-0.46
-0.40
-0.22
-0.40

APPENDIX III Weight % Total Carbon

Bed #	Sample #	% Total Carbon
23	29H	0.15
	30E	0.40
	32BB	0.10
	36F	0.29
	30AA	0.89
	27E	0.34
	27I	0.15
	26G	0.29
	29I	0.10
	34D	0.28
	33AA	0.17
	32G	0.51
	35G	0.24
26	34G	0.262
	25H	0.182
	27H	0.336
	29AA	0.288
	27E	0.377
	29B	0.337
	29G	0.348
	25F	0.294
	30AA	0.340
	35I	0.364
	34J	0.338
	30E	0.399
	34D	0.380
	33AA	0.326
	33A	0.331
	28H	0.545
	31BB	0.281
43	32G	0.844
	29G	0.440
	35G	0.720
	23H	0.640
	26E	0.366
	30E	0.161
	33I	0.251
	27I	0.167
	28H	0.690
	26G	0.493
	35I	0.995
	30H	0.571

APPENDIX III cont'd

Bed #	Sample #	% Total Carbon
43	25H	0.256
	27H	0.506
	29H	0.506
	30G	0.311
	28I	0.752
Cupriferous Zone Adjacent to the Transition Zone		
upper #43	27L	0.444
upper #46	34-1/4C-3/4	0.352
lower #46	34-1/2I-1/2	0.386
upper #46	29-1/4J	0.292
upper #46	32-1/8J	0.316
lower #44	27L	1.160

APPENDIX IV Weight % Sulphide

Bed #	Sample #	% Sulphide
23	27E	1.748
	30AA	1.970, 1.996
	30E	1.459
	26G	1.760
	27H	0.763
	23H	0.955
	29AA	1.537
	25F	1.895
	35H	0.565
	27C	1.737
	26F	0.266, 0.268
	34G	1.150
	33I	0.693
	30A	1.736
	29F	1.325
	32I	0.281, 0.297
	27L	0.735
	29D	1.333
	35I	1.227
	30H	0.924, 0.933
	31K	0.540
	30G	0.341
	34D	0.561
	29H	0.793
	36F	0.803
	27I	0.506
	32BB	0.607
	31BB	0.644
	32G	0.721
	33AA	0.619
	35G	0.660
	29I	0.315, 0.316
26	32G	1.467
	36F	0.682
	32BB	0.474
	29B	0.450
	31BB	0.365, 0.287, 0.271
	28H	0.435
	31K	1.132
	35I	0.643
	27H	0.654
	29G	0.504
	25F	0.728
	27E	0.910
	30H	0.648

APPENDIX IV cont'd

Bed #	Sample #	% Sulphide
26	29AA	1.832
	34J	0.464
	33AA	0.496
	32I	0.568
	30E	0.917
	34G	0.550
	30AA	0.543
	33A	0.369
	34D	0.740
43	27H	2.207
	23H	1.545
	29G	1.327
	35G	2.234
	31K	0.755
	30H	1.290
	29J	1.320, 1.330
	28H	1.974
	33I	0.579
	32G	1.864
	28I	1.765, 1.743
	26G	2.230
	26F	1.680
	29I	1.589
	25F	0.566
	27L	1.610
	26E	1.600
	29H	2.301, 2.210
	27I	0.677
	35I	1.110
	30E	0.480
	25H	1.207
	30G	1.152

Cupriferous Zone Adjacent to the Transition Zone

#46	34-1/4C-3/4	1.124
lower #44	27L	2.541
#46	30H	0.534
upper #43	27L	2.411
upper #46	33-1/4F-1/8	0.014
upper #46	29-1/4J	0.761
lower #46	34-1/2I-1/8	0.353

APPENDIX V Boron Analyses

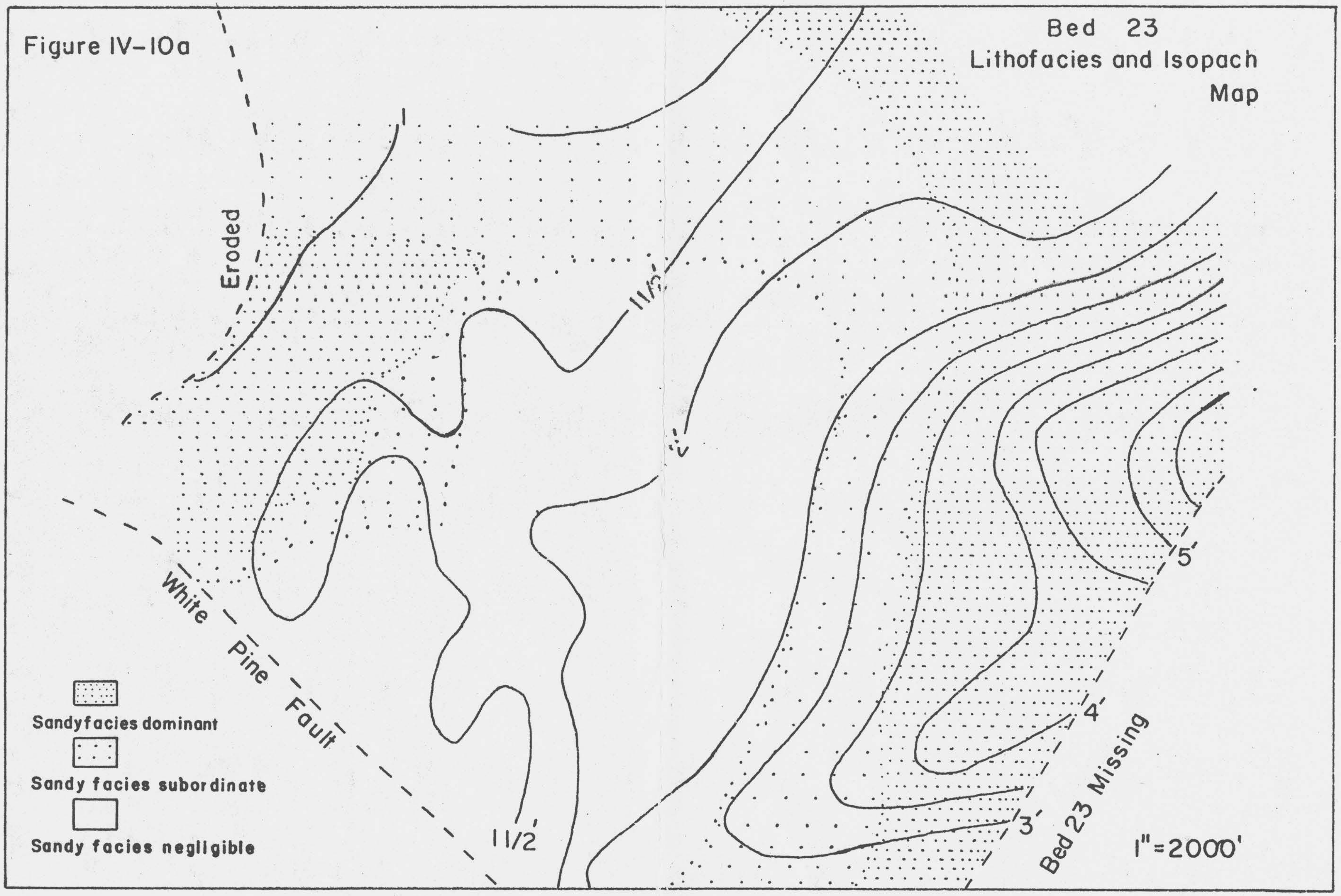
Bed #	Sample #	ppm Boron		Av. Boron	% Chlorite + Less than 2u fraction	
23	29H	32	37	35	52	49
	32BB	42	46	44	37	
	36F	66	81	74	51	
	27I	39	45	42	38	
	32G	22	32	27	42	42
	27E	74	59	67	51	
26	27E	65	87	76	48	50
	31BB	81	76	79	53	54
	34G	59	81	70	52	
	35I	35	58	47	47	
	29AA	54	50	52		
	29G	66	81	74	53	51
43	36F	87	83	85	47	50
	28I	80	80	80	55	
	23H	100	96	98	57	57
	26E	85	100	93	56	
	29G	54	76	65	48	48
	29H	63	71	67		

Pyrite Zone Adjacent to the Transition Zone

U. #44 - L. #46	23G	59	60	60
#50	33D	72	69	71
upper #46	33-1/4F-1/8	65	62	64
upper #46	34-1/4C-3/4	58	46	52
upper #46	34-1/4C-3/4	62	71	67

Figure IV-10a

Bed 23
Lithofacies and Isopach
Map



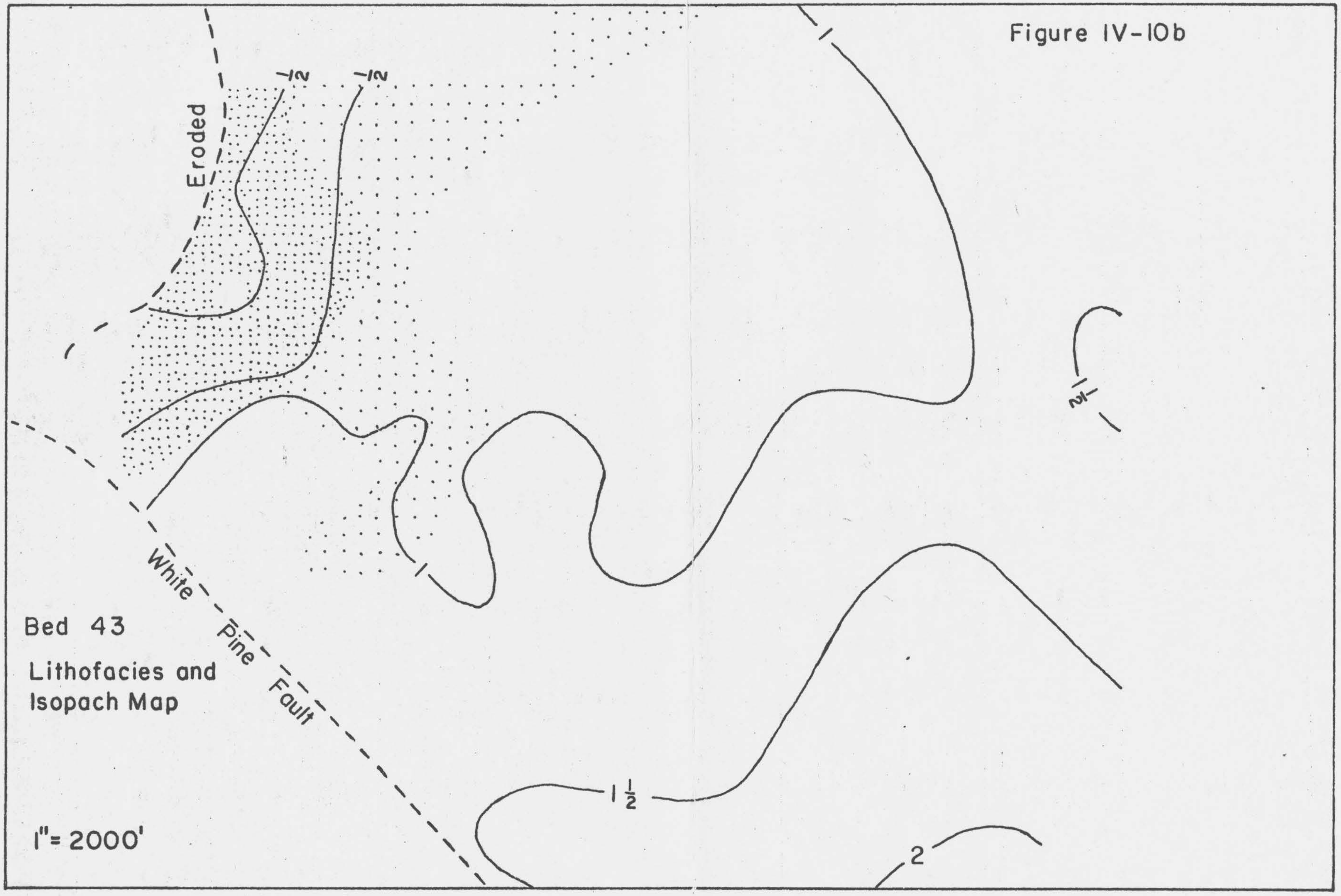


Figure IV-10b

Bed 43

Lithofacies and Isopach Map

Figure IV–10c'

⁝

Coarsest bed is medium-grained sandstone
(1/4–1/2 mm)

⁙

Coarsest bed is coarse-grained sandstone
(1/2–1mm)
Average bed is fine–grained sandstone
(1/8–1/4 mm)

░

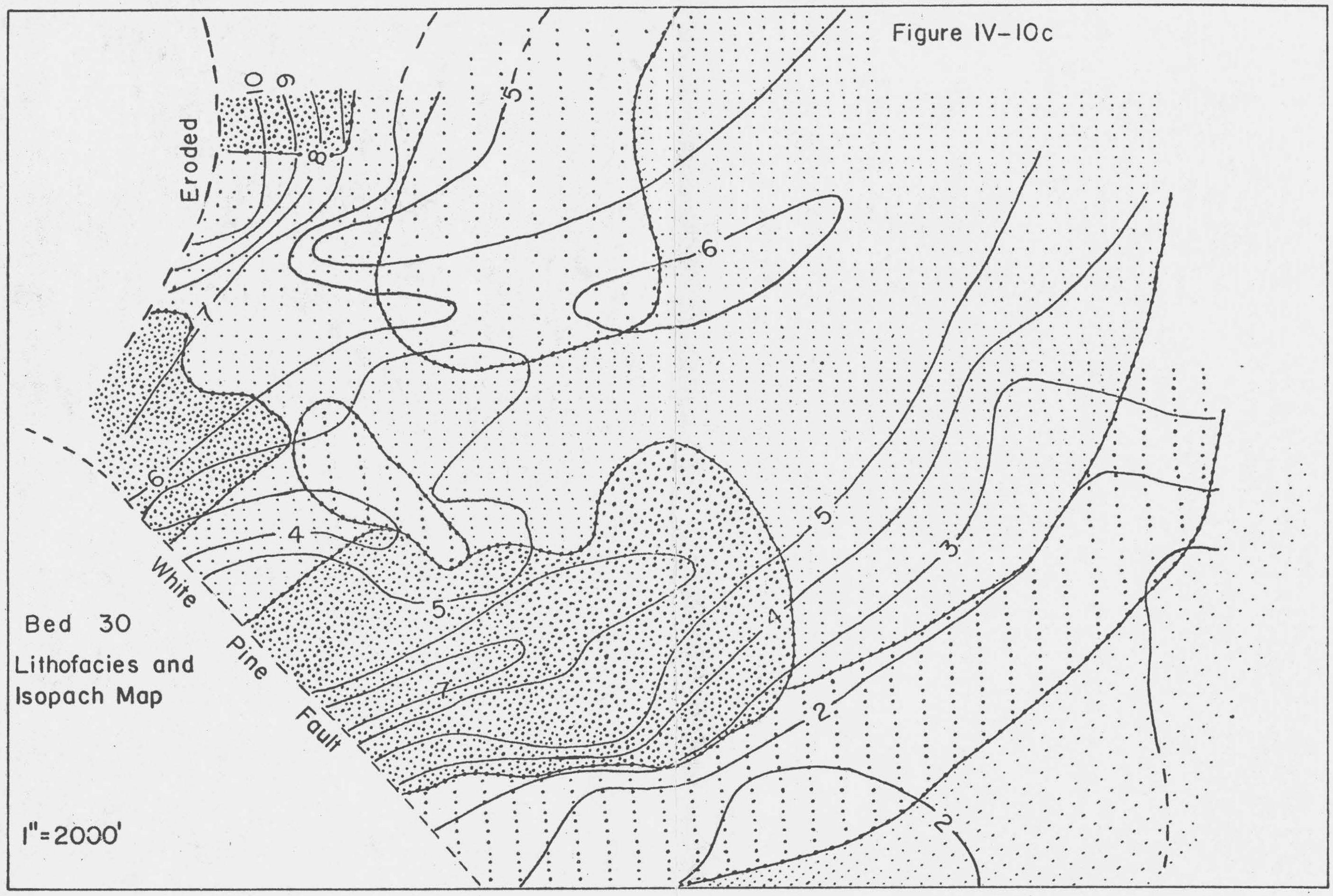
Coarsest bed is fine-grained sandstone
(1/8–1/4 mm)

▒

Coarsest bed is coarse–grained sandstone
(1/2–1mm)
Average bed is medium–grained sandstone
(1/4–1/2 mm)

Legend for Figure IV–10c

Figure IV-10c



Bed 30
Lithofacies and
Isopach Map

1" = 2000'