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AN INVESTIGATION OF THE MINERALOGY AND PETROGRAPHY OF URANIUM-BEARING SHALES

Consists of Thesis: AN INVESTIGATION OF THE RELATIONSHIPS BETWEEN SELECTED MINERALS, TRACE ELEMENTS AND ORGANIC CONSTITUENTS OF SEVERAL BLACK SHALES

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AN INVESTIGATION OF THE MINERALOGY AND PETROGRAPHY OF URANIUM-BEARING SHALES

Thomas F. Bates - Project Director

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Department of Mineralogy
College of Mineral Industries
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The Pennsylvania State University

The Graduate School

Department of Mineralogy and Petrology

An Investigation of the Relationships Between Selected Minerals, Trace Elements and Organic Constituents of Several Black Shales

A thesis in

Mineralogy and Petrology

by

Erwin O. Strahl

Submitted in partial fulfillment
of the requirements
for the degree of

Doctor of Philosophy

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ABSTRACT

The relationships between and among the mineral, organic, and trace element constituents of samples of the Chattanooga and the Ohio shales in the United States, the St. Hippolyte of France, and the Alum shale of Sweden have been investigated and discussed in terms of the geochemical environments. The relative importance of the environmental factors was evaluated.

A total of 280 samples were analyzed for total carbon, organic carbon, aliphatic and aromatic hydrocarbon, carbonate, total iron, iron oxides, pyrite, total silicates, quartz, kaolinite, illite, amorphous silicates, uranium, molybdenum, manganese, and quartz grain size.

The methods for the analysis of the hydrocarbons, the silicate minerals and molybdenum and manganese were developed or improved by the writer in order that suitable quantitative data could be obtained.

The amounts of aromatic and aliphatic hydrocarbons obtainable from a shale by CS_2 extraction were determined by nuclear magnetic resonance spectroscopy.

The amounts of quartz, kaolinite, illite, and amorphous silicates were determined by first roasting and acid leaching the samples and then obtaining x-ray diffractometer tracings.

The molybdenum and manganese were quantitatively determined by using a method which combined the advantages of solution - spark and mutual standard emission spectroscopy.

The data obtained were analyzed using correlation and factor analysis statistics.

The more important relationships made obvious by this investigation are as follows:

Pyrite, organic carbon, and uranium vary together in the shales studied and depend upon reducing conditions for their concentration.

Molybdenum and manganese co-precipitate in an environment characterized by the presence of carbonate minerals. The presence of carbonate is a reflection of the oxidative environment necessary to precipitate these elements.

In a highly reducing environment, organic carbon and carbonate are incompatable but in a more oxidizing environment the enrichment in organic carbon is paralleled by an enrichment in carbonate.

In the marine shales investigated, the amount of illite relative to the amount of kaolinite is much greater than in the continental shale.

A well defined negative relationship between illite and amorphous silicates in the marine shales, and a poorly defined negative relationship between kaolinite and amorphous silicates in the continental shale, was found. In both the marine and continental shales, such relationships are considered to be a function of the rate of deposition.

As the amount of quartz in the sediment increases, the maximum quartz grain size also increases, but the increase in grain size for a given increase in amount is more rapid in the continental shale than in the marine shales.

The redox environment is the most important factor in the deposition of black shales. The rate of deposition appears to be highly interrelated with the redox environment in those cases where the rate of deposition was relatively rapid.

As shown by the relationship of aliphatic to organic carbon, the organic material is uniform in character in the bituminous shales and somewhat more variable in the carbonaceous shales.

On the basis of this study, it is concluded that the compositions of the shales investigated are highly dependent on the geological factors of environment. The redox potential; the nature of the basin of deposition, marine or continental; and the rate of deposition apparently control the mineralogical and chemical compositions of the black shales. The nature of the organic material, bituminous or carbonaceous, appears to be related to both the type of material available and to the oxidation of the sediment during deposition.

These geological factors are interrelated and the composition of a shale is the result of the joint action of these factors during deposition.

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Special thanks are due Mr. Robert O'Neil for his patience and suggestions relating to the analysis of the samples, and to Mrs. Mary Selander for her aid in the preparation of the data for analysis.

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INTRODUCTION

REVIEW OF PREVIOUS WORK

General

Shales comprise approximately 90% of all sedimentary rocks (Goldschmidt, V. M., 1933) and are perhaps the least thoroughly studied of all sediments.

Krumbein and Sloss (1953) define shales as "fine-grained, laminated or fissile sedimentary rocks with a predominance of detrital components" Grim (1953) states that shales must have a distinct laminated or layered character but that the term is loosely used by many workers to include fine-grained sediments void of apparent lamination.

Grain size is the most commonly accepted criterion for recognizing a shale. Most authors agree that the grains of a shale vary from silt size to clay size. According to Krynine (1948) detrital sediments which have a grain size of less than 0.0625 mm and which are unctuous to the touch are to be classified as shales.

Krumbein (1947), who empirically determined the grain size distributions of shales, states that "...the grain size of shales averages from 0.062 mm to 0.004 mm" and that "...the grain size distribution is usually skewed toward the finer sizes".

The Composition of Shales

Mineral Composition

The major mineral components of shales are usually clay minerals and quartz, but the other mineral components may be as varied as those found in the coarser sedimentary rocks. Several species of the clay minerals (including chlorite) are found in nearly every shale and the variation in the relative abundance is often taken as an indication of source or environment of deposition.

Under conditions of rapid deposition, the clay minerals are not appreciably altered and can be used to indicate the source of the detrital material. From an intensive study of the mineralogy of argillaceous sediments of the central United States, Weaver (1958a) concludes that the clay minerals of these states are quite similar to those of the source material and not appreciably affected by the environment of deposition. Milne and Earley (1958) found as a result of a study of recent sediments of the Gulf Coast area that both the source and the environment of deposition are important factors in determining the clay mineral assemblage of a mud. In a summary of their work they state:

> "The clay mineralogy of sediments in the later stages of geologic history appears to vary between two extremes in which either montmorillonite or kaolinite predominates. The evidence which has been presented suggests that climate in the source area may be the most important factor in determining the resultant clay mineral assemblage. It has been observed that illite may be formed in a depositional area where the rate of sedimentation is slow. Organic material which may be complexed with montmorillonite in fresh water environments is altered or no longer associated structurally with the clay in sea-water environments. The compaction apparently produces very little alteration of the clay minerals except possibly in the exchange ions."

Generalizing their findings they state:

> "Alteration of clay minerals in a depositional area can be expected where the sedimentation rate is low and sufficient time is available for chemical equilibria

> between sea water and the clay minerals. In areas of rapid mud deposition, the blanketing effect of overlying clay material probably reduces the chemical interaction to that which is possible between the clay and the entrapped water."

The work of Grim, Dietz and Bradley (1949), Grim and Johns (1954), Powers (1954), and Griffin and Ingram (1955) on Recent marine sediments, as well as the work of Murray (1953), Keller (1956), and Degens, et al, (1957) on ancient marine sediments provides evidence that there is some development of illite as sediments pass into a marine environment. Grim (1958) in recognizing the presence of clay minerals other than illite in marine sediments states:

> "There is no doubt that the transition to illite in the marine environment is not complete. This is abundantly proved by the presence of other clay minerals in ancient marine sediments. It seems to the writer that the presence of kaolinite, montmorillonite, and mixed-layer structures in ancient marine sediments does not, in the face of the other evidence already stated, indicate that there is no change whatever when sediments pass from a fresh-water to a marine environment. It means only that the change is incomplete."

In the same paper, while summarizing some of his work on the Claiborne sands of the Eocene of Mississippi, Grim cites an example of an illite type clay mineral that developed directly in a marine environment from a siliceous amorphous initial material.

Weaver (1958), in a discussion of the origin and significance of clay minerals in sedimentary rocks, summarizes recent data on marine black shales in the following manner:

> "Marine black shales rich in organic matter and pyrite are rich in illite and mixed-layer illite-montmorillonite and seldom contain kaolinite."

The presence of small amounts of kaolinite has been noted in several marine black shales (Duey, 1957; Bates and Strahl, 1957, 1958). In the Chattanooga shale the kaolinite was found to be located within the nodules and lenses of authigenic pyrite which are common in the sediment. Dolsen (1957), in a comprehensive study of the pyrite concentrates of the Chattanooga shale, found that the presence of kaolinite was limited to the pyrite concentrates associated with calcite. In the light of existing information on the distribution of kaolinite in sedimentary rocks as summarized by Rankama and Sahama (1950, p. 205) and by Fredrickson (1952) this kaolinite is probably formed in situ and is not of detrital origin.

Among the minor constituents, pyrite and carbonates are common to most shales. Pyrite is abundant in marine black shales whereas carbonate is usually found only in small quantities.

The presence of pyrite in black shales is generally believed to reflect the highly reducing environment of sediments rich in organic material.

The iron is carried to the basin of deposition either as ferrous bicarbonate ($Fe(HCO_3)_2$) or as a ferric hydroxide ($Fe(OH)_3$) colloid (Goldschmidt, 1954). Upon settling in an organic-rich basin of deposition the ferric hydroxide colloid is reduced by the hydrogen sulfide produced during the decay of sulfur-bearing organic compounds (or sulfur producing bacteria) and pyrite is formed. Ferrous bicarbonate is precipitated as siderite ($FeCO_3$) when the carbon dioxide is removed from solution by either an increase in temperature or the process of photosynthesis.

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Precipitated ferrous carbonate (siderite) is often found in bogs. However, ferrous bicarbonate is unstable in oxygenated water and rapidly decomposes into ferric hydroxide and carbon dioxide (Rankama and Sahama, 1950, p. 663). Under extreme reducing conditions all the ferric iron would be reduced to the ferrous state but in the variable natural environment a variable quantity would remain as ferric hydroxide and during diagenesis alter to ferric oxide.

In addition to siderite, the carbonate mineral calcite ($CaCO_3$) is a common minor constituent of shales. The CO_2 needed to produce the calcite is obtained from carbonated solutions entering the basin of deposition and from the oxidation of organic material within the basin. However, only small quantities of calcite are generally found in black shales because in the stagnant bottom muds the carbon dioxide is largely consumed by a reaction with hydrogen to produce methane.

Quartz, a major mineral constituent of shales is generally thought of as a detrital mineral but occurrences of syngenetic quartz in limestones are common. In shales deposited at a rapid rate the likelihood of accumulating even small quantities of authigenic quartz is small, but in organic rich shales which were deposited at a low rate appreciable quantities of quartz (as well as illite) could be formed from solutions and colloids (Correns, 1949; Mason, 1952).

Organic Composition

Shales are generally classified on the basis of color. The organic-rich shales are gray to black in color and are further classified on the basis of the type of organic material they contain, the two main classes being bituminous and carbonaceous shales.

A bituminous shale or oil shale is described by Boone (1952) as a shale containing hydrocarbons or bituminous material. Tomkeieff (1954) further defines a bituminous shale as a fine-grained, black or dark brown shale containing sapropelic material.

A carbonaceous shale as described by Boone (1952) contains small particles of coal or carbon distributed throughout the shale.

Twenhofel (1939) also defines the nature of the organic material in both shale types. He considers the organic material in bituminous shales as "more or less composed of fatty algae, spores, spore cases, pollen grains, resin, and similar materials," and in carbonaceous shales as "composed of a dominance of visible plant material which was originally cellulosic or ligneous".

The difference in the nature of the organic material between these two shale types implies a different source of the organic material for each type. The differences are, however, amply explained by Rankama and Sahama (1950, p. 232) who state:

> "Biochemical processes often participate in the production of oxidizing or reducing environments. They may even dominate therein. When green plants synthesize organic compounds, molecular oxygen is liberated. It is responsible for the high redox potential on the Earth's surface. On the other hand, the organic matter, during its decay, creates very low redox potentials. The principal gaseous products of the bacterial decomposition of organic matter in a reducing environment are hydrogen sulfide, methane, and possibly other volatile hydrocarbons. Only little carbon dioxide is formed. The reducing conditions are maintained by the presence of certain organic and inorganic compounds, e.g.,

> sulfoproteins, ferrous iron, manganous manganese, and hydrogen sulfide. Therefore, the conditions favor the hydrogenation of organic matter and the formation and preservation of petroleum hydrocarbons. Under oxidizing conditions, on the other hand, the micro-organisms tend to carbonize organic matter, the last stage of the process being the formation of coal, or to oxidize it to carbon dioxide."

In black shales, therefore, the nature of the organic material can be considered to vary continuously between bituminous and carbonaceous material. Duey (1957), in comparing the mineralogy and chemistry of the Allegheny shales to that of the Chattanooga shales, states:

> "The fact that many authors have observed shales which have intermediate properties between these shales suggests that carbonaceous and bituminous shales should be considered theoretical end members in a transitional series."

Trace Element Composition

The concentration of certain trace elements in shales is well established. Bituminous shales are known to be effective concentrators of the elements which precipitate under reducing conditions by a change in valence state or combination with sulfur to form sulfides. According to Mason (1952, p.153), the elements commonly found to be enriched in bituminous shales are: V, U, As, Sb, Mo, Cu, Ni, Cd, Ag, Au, and metals of the platinum groups. The same elements are found to be concentrated in carbonaceous shales but in lesser amounts. There is also some concentration of manganese in bituminous shales but it is often not appreciated because of the greater concentrations of this element found in carbonaceous shales (Duey, 1958).

Of these elements, uranium, molybdenum, and manganese are perhaps the most interesting because of their polyvalent nature and methods of precipitation.

The form of U in sea water is not known with certainty. In acid solutions it is present as the divalent uranyl cation, but with increasing alkalinity uranate ions are also present (Goldschmidt, 1954).

In the reducing environment of organic rich shales the uranium contained in solution is reduced to the quadrivalent form and precipitated. The ionic potential (ratio of charge to ionic radius) of quadrivalent uranium would indicate that reduced uranium might precipitate as the hydroxide, but there is a possibility that it may have been adsorbed by the organic material.

It has been suggested by Goldschmidt (1954) that uranium upon precipitation would be adsorbed on the carbonaceous material or even collected into the viscous hydrocarbons formed from the hydrogenated organic material. Breger and Schopf (1954) have suggested that uranium may form organo-metallic compounds in the presence of bituminous material, and McKelvey and Nelson (1950) conclude that "the uranium may be held by ion exchange adsorption on organic or clay minerals". McKelvey, Everhart, and Garrels (1955) summarize the state of knowledge of uranium in black shales as:

> "The manner of, and conditions favoring precipitation of uranium in the black shales are difficult to decipher, particularly because it is possible, even likely, that the uranium in the black shales now is in a form or association different from that at the time of deposition. Deposition may have taken place in either or both of two ways: 1) chemical adsorption by organic

> matter (living or dead) or 2) direct precipitation. Some marine algae concentrate minor metals and dead plankton is reported to be an effective adsorbent for uranium and other metals.
>
> The presence of uranium in rocks containing the largest amounts of organic matter and pyrite in the shale sequence and its apparent concentration in embayments like those in the alum shale, suggests that the precipitation of uranium may be controlled by redox potential. According to Goldschmidt (1954, p. 566), precipitation of uranium in black shales "might result from a reduction of sexivalent uranium to the quadrivalent stage by the action of hydrogen sulfide in stagnant bottom waters....We may therefore expect accumulation of the solute uranium from sea water by re-precipitation in areas where strongly reducing conditions prevail." The general solubility relationships of U^{+4} and U^{+6} already described confirm this view, but the absence of any uranium mineral in the black shales suggests that uranium did not precipitate as a definite uranium compound, even under reducing conditions. Although it thus seems more likely that the uranium was adsorbed by organic matter or other collodial materials, conditions that favored the chemical precipitation of uranium would also have favored its removal from solution by chemical adsorption.
>
> Anyone who has worked with black shales or studied the results of their uranium analyses cannot help asking and being baffled by the question as to why one shale layer contains a much different concentration than another when both appear closely similar if not identical in composition. The answer to this question may lie in Eh-pH control. The close relation between maximum amounts of uranium, oil, total organic matter and sulfides in the alum shale suggests that appreciable deposition of uranium takes place only when the pH and Eh lie within narrow limits--limits that may be approached closely enough in the deposition of ordinary black shales to permit the formation of sulfides and the preservation of organic matter, but are reached only rarely. Perhaps the amount of uranium in the sea at the time of deposition, or the length of time the shale consatituents were exposed to the sea-water before burial also influenced the amount of uranium present in individual beds. Other factors also might account for the variation in uranium content of the black shales but these factors are unknown now."

The writer and Bates (Bates and Strahl, 1958) have since shown that the variation in uranium content in both carbonaceous and bituminous shales can be largely accounted for by the variation in the sedimentary environment as reflected by the quantitative variation of the major mineral constituents and carbon.

Manganese is carried in solution as manganese bicarbonate. In an oxygenated environment it is oxidized and precipitated as $Mn(OH)_4$. The $Mn(OH)_4$ then slowly converts to manganese dioxide (MnO_2). The presence of decaying organic matter, however, limits the oxidative conditions and the manganese is retained in the mobile manganous form (Goldschmidt, 1954, pp. 637-8). The presence of appreciable quantities of MnO_2 in carbonaceous sediments and its limited concentration in bituminous sediments may then be attributed to the more oxidative environment of carbonaceous shale deposition.

Under the relatively severe reducing conditions of bituminous shales, the manganese may be concentrated as manganese sulfide but it is rarely reported in the literature.

The manner in which molybdenum goes into solution is similar to that of uranium. Under strongly oxidizing conditions molybdenum, as the molybdate ion, is highly mobile. Under reducing conditions, in water containing considerable amounts of H_2S, the precipitation of molybdenum as MoS_2 should be expected. According to Rankama (1948) "....bituminous and sapropelic sediments contain notable amounts of molybdenum as sulfide (140 g/ton Mo)." The behavior of molybdenum in sediments is complex. This element, like uranium, should be primarily concentrated in the highly reducing bituminous sediments, but Goldschmidt (1954, p. 560) reports:

> "A precipitation of molybdenum takes place in ordinary hydrolyzate sediments and perhaps still more obviously in oxidate sediments, especially in those rocks and minerals in which trivalent and quadrivalent manganese is being precipitated. In the course of many years of experience of x-ray spectrography, the author has always found quite conspicuous amounts of molybdenum in manganese dioxide minerals or from other deposits of the zone of oxidation. The amounts are generally of the order of several tenths of 1 percent Mo down to some hundredths of 1 percent. Even the manganese dioxide minerals from deep sea sediments contain remarkable amounts of Mo originating from the content of the element in sea water."

PURPOSE

It has been frequently noted in the literature that environment plays an important role in the deposition of various constituents of black shales. The investigations reported, however, were limited to the study of the relationship of the environment to single or isolated groups of mineral, organic, or chemical constituents. The primary purpose of this investigation is to study the relationships between and among the mineral, organic, and chemical (trace element) constituents and then to evaluate these relationships in terms of the geochemical environment.

In order to accomplish this goal, three secondary objectives had to be attained.

1) The first and most important of these was to design new or modify existing techniques for the analysis of samples. The techniques used by other workers for the analysis of the silicate minerals, organic constituents, trace elements, and grain size were found to lack precision

and consistency or were not applicable to the study of a large number of samples.

Silicate Mineral Analysis

Since in preliminary experiments only imprecise and inconsistent clay mineral analysis could be obtained from existing x-ray techniques, a new method of sample preparation and x-ray analysis had to be devised.

Organic Material Analysis

Fractional distillation and chromatographic analyses were found impractical for the analysis of a large number of samples. Since the applicability of Nuclear Magnetic Resonance Spectroscopy to the qualitative analysis of hydrocarbons had been demonstrated, an important objective of the present work became to develop precise quantitative techniques and use them to obtain data on the samples under study.

Trace Element Analysis

The existing methods of spectrographic analysis for trace elements did not have the sensitivity or precision required for this investigation. A method combining the advantages of spark, solution, and mutual standards had to be developed and applied.

Grain Size Analysis

The sedimentation methods used for grain size analysis are highly inaccurate for shales since black shales cannot be completely disaggregated without altering the particle size.

Existing thin section methods were not feasible since, of all the material present, only the largest quartz grains could be clearly resolved. As a result the thin section methods had to be modified to utilize only these grains.

2) The second subsidiary objective was to analyze a large number of shale samples from several different black shales.

Since the approach of this investigation is empirical and quantitative, the relationships between variables are best studied statistically. To accomplish this an adequately large number of samples had to be analyzed from each shale. In order to generalize the results, several shales had to be studied.

3) The third subsidiary objective was to summarize the data through the use of correlation and factor analysis statistics.

SCOPE

This study was primarily designed as a quantitative investigation of the minerals, organic components, and trace elements of a large number of black shales. It was found necessary, however, to devote considerable effort to the designing and modification of analytical procedures because the methods commonly used for silicate minerals, organic material and trace element analysis did not give the accuracy or precision necessary for this study or were not practical for the analysis of a large number of samples.

The number of samples ultimately chosen for analysis, therefore, had to be limited to approximately 280. Practical considerations also limited the number of shale formations studied to those from which relatively unweathered drill core samples are available and for which the qualitative mineralogy was adequately described. The shales chosen for study were: the Chattanooga (120 samples) and the Alum (60 samples), bituminous marine shales; the Ohio (50 samples), a bituminous to carbonaceous marine shale; and the St. Hippolyte (50 samples), a carbonaceous continental shale.

In addition to the compositional measures already mentioned, a textural measurement, quartz grain size, was made on each sample to provide information on the relationship between composition and the grain size of the shale.

The analysis of the data was accomplished through the use of correlation statistics and the principle axis method of factor analysis in order to determine the interrelationships of the constituents and to evaluate them in terms of the geochemical environment.

EXPERIMENTAL PROCEDURES

INTRODUCTION

The drill cores of the four shales, the Ohio, the St. Hippolyte, the Alum and the Chattanooga were sampled, prepared for analysis, and qualitatively described prior to this investigation. One of these shales, the Chattanooga, was sampled in a pattern designed to encompass known regional variations in composition (Bates, et al, 1956).

The mineralogy of the four shales was found to be quite similar. The mineralogy of the Chattanooga shale is described in detail by Bates and Strahl (1957). Briefly, illite and quartz are the major constituents and pyrite, kaolinite, and calcite occur in minor amounts along with small quantities of the minerals chlorite, apatite, zircon, rutile, and tourmaline. Qualitatively, the Ohio and Alum shales are of similar composition (Bates and Strahl, 1958) but the St. Hippolyte shale differs in that the carbonate mineral is siderite and minor quantities of meta-autunite are occasionally present.

The samples were analyzed by wet chemical, fluorimetric, x-ray fluorescence, x-ray diffraction, emission spectrographic, nuclear magnetic resonance spectrographic, and grain size analysis techniques. Many of the analytical methods were designed or modified specifically for this investigation by the writer, or for the study of fine grained sediments by O'Neil (1958). The wet chemical, fluorimetric, and x-ray fluorescence analyses were performed by technical assistants under the direction of Mr. Robert L. O'Neil during the same period as the remaining analyses were performed by the author.

The analysis of data has been accomplished largely by the application of correlation and factor analysis.

SAMPLING

The source, location, geologic age and method of sampling of each shale is given below.

1) Ohio Shale

Geologic age:	Devonian
Type:	Bituminous to carbonaceous marine
Location:	Located in field at intersection of Harris road and tracks of the Nickel Plate R. R., about 1 mile south of U. S. Highway 6, elevation 620', cored from 30' to 800'. Core #560, International Salt Co. test #6, Lorain County, Sheffield Twp., Ohio.
Source:	Mr. George Shearrow, Ohio State Geological Survey, Columbus, Ohio.
Sampling:	Sampled by the writer at Ohio State University. Samples taken at random to provide 1 sample for every 2.5 feet of core.

2) St. Hippolyte Shale

Geologic age:	Carboniferous
Type:	Carbonaceous continental
Location:	Ten drill cores from the vicinity of St. Hippolyte, Vosges Mountains, France.

Source: M. Jacques Mabile, The Director of Research and Mineral Exploration, Atomic Energy Commission of France.

Sampling: Each of the ten cores was randomly sampled by the staff of the French Atomic Energy Commission to provide a total of 150 samples.

3) Alum Shale

Geologic age: Cambrian

Type: Bituminous marine

Location: Core number III, 7.73 - 25.60 meters, from the locality Norra Mossby, District of Narke (Kvantrop), Sweden.

Source: Dr. Roland Rynninger, Aktiebolaget Atomenergi, Stockholm, Sweden.

Sampling: Randomly sampled by the writer to provide 118 samples out of the 59' drill core.

4) Chattanooga Shale

Geologic age: Lower Mississippian

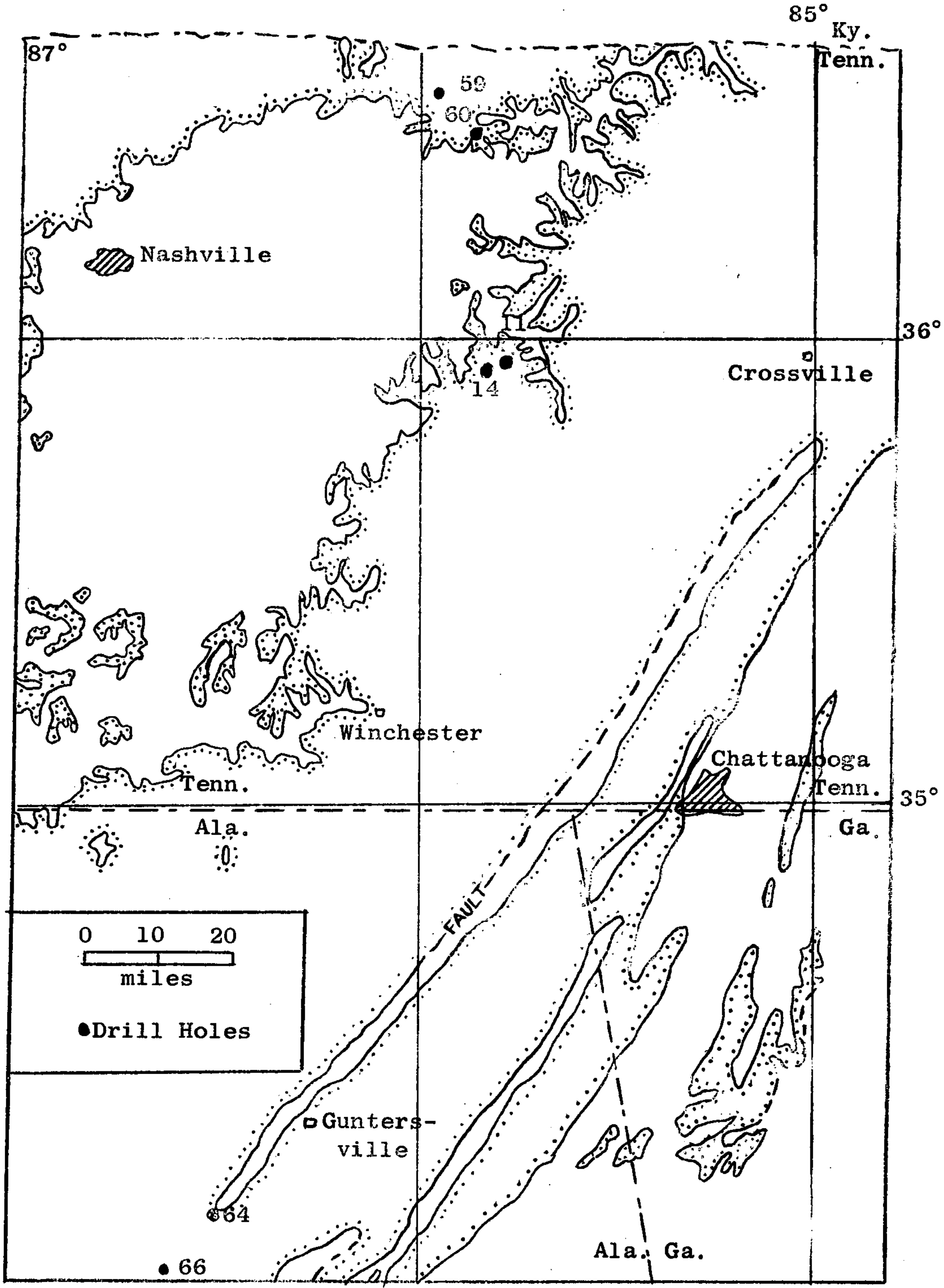
Type: Bituminous marine

Location: Locations of the drill cores (YB-11, YB-14, NV 59, NV 60, Al 64, Al 66) are given in figure 1.

Source: U. S. Geological Survey and U. S. Bureau of Mines. Cores were logged by T. M. Kehn and Julien Sorren of the U. S. Geological Survey.

Figure 1

Areal Distribution of Chattanooga Shale Drill Cores



Sampling: The shale has been stratigraphically divided into 2 members, the Gassaway (upper member) and the Dowelltown (lower). Only the Gassaway member was sampled. Samples were randomly chosen by the writer. The number of samples was fixed at: length of core in feet x 2.

The sample size was approximately 1/2 inch of a quartered 2 inch drill core. A thin section was cut from each sample and the remainder ground to pass 100 mesh.

This sampling provided 640 samples for analysis. However, since the analytical procedures adopted in this study were found to be too time-consuming to allow for a complete analysis of all samples, the number of samples was reduced to 280: 50 samples of the Ohio shale, 50 samples of St. Hippolyte shale, 60 samples of the Alum shale and 120 samples of the Chattanooga shale. A combination of random and grab sampling was used to obtain the 280 samples.

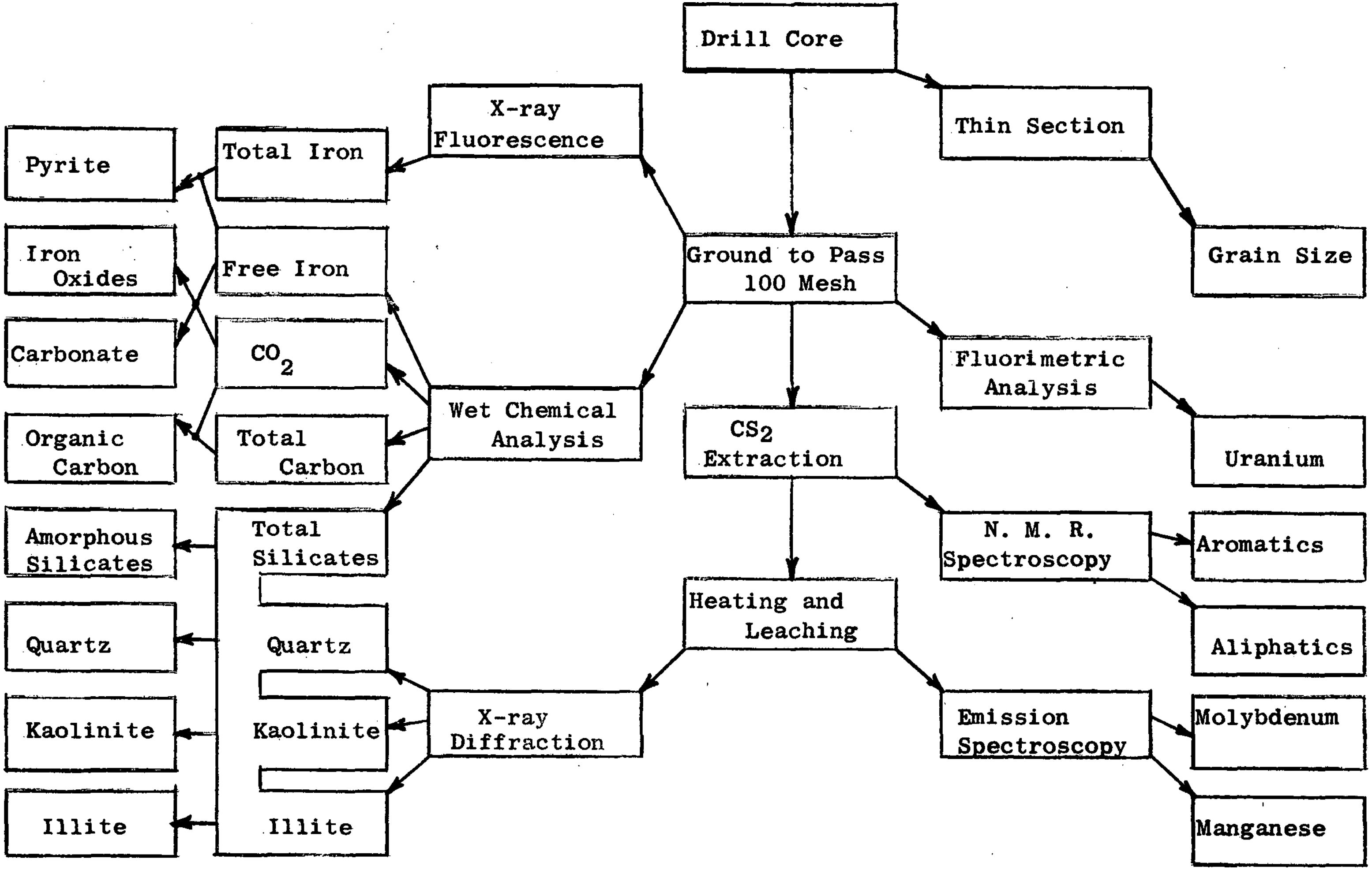
ANALYSIS OF SAMPLES

Introduction

The procedure followed for the analysis of samples is shown diagramatically in figure 2. For convenience the analyses are discussed in five sections; chemical analyses, organic material analysis, silicate mineral analysis, spectrochemical analysis and quartz grain size analysis.

Figure 2

Flow Sheet for Analysis of Samples



Chemical Analyses

Introduction

The analyses discussed in this section include the fluorimetric determination of uranium, x-ray fluorescence measurement of iron, and chemical determinations of total carbon, carbonate carbon, free iron, and total silicates. The chemical data obtained by these analyses were recalculated to give the amount of organic carbon, calcite, siderite, pyrite, and iron oxides. The analyses were performed by the staff of the AEC project that supported this research under the guidance of Mr. Robert O'Neil, project analyst. The procedures used were designed for the analysis of fine grained sedimentary rocks by Mr. O'Neil.

Total Iron

Total iron was determined by x-ray fluorescence procedures on a General Electric XRD-3 unit, equipped with a lithium fluoride analyzer, tungsten target tube, and fluorescence sample holder box. The tube was operated at 50 KV and 2 ma. A fixed number of counts was taken at the iron $K\beta$ peak at 57.50° 2θ (for LiF) and of the background at 60.0° 2θ. A calibration curve was used to convert the counts per second into percent iron. The precision was ± 2% (2s) of the determined value (O'Neil, 1958, pp. 25-27).

Free Iron

Free iron was taken as the amount of iron which can be leached from a sample by HCl at a temperature of 85°C. This method measures the amount of oxide and carbonate iron but does not take account of the sulfide iron. The following procedure was used: The roasted shale is digested at 85°C for 2 hours in 1:1 HCl. The digestate is filtered, washed with 1:20 HCl, the filtrate heated to boiling and stannous chloride added to reduce the iron. The solution is cooled to room temperature and titrated with potassium dichromate in the usual manner (Strahl, et al, 1954, pp. 27-29).

Carbonate Carbon

The carbonate was determined as the amount of CO_2 liberated in hot dilute phosphoric acid. The procedure used is as follows: The sample is placed in a flask to which 1:4 phosphoric acid is added through a valve. The contents of the flask is heated to boiling for 3-5 minutes and the evolved CO_2 absorbed in a caroxite filled trap (O'Neil, 1958, pp. 24-25).

Total Carbon

The total carbon is determined by heating the sample to 900°C in an organic combustion train. In this method the carbon is oxidized to CO_2 and the carbonate minerals are decomposed and the evolved CO_2 absorbed in a caroxite filled Nesbitt tube (O'Neil, 1958, pp. 20-21).

Total Silicates

The quantity of total silicates was taken as the residue after roasting and leaching. The sample was heated to 450°C for 12 hours and then digested for 1 hour in 1:1 HCl. The weight of the residue was taken as the weight of the silicate fraction of the sample (Strahl, et al, 1955, pp. 31-32).

Uranium

Uranium is analyzed fluorimetrically as described by Grimaldi and Levine (1954). The sample is first digested with HNO_3 and HF, the HF is removed by repeated evaporations with 1:1 HNO_3. The residue is treated with 1:1 HNO_3 until all soluble salts are in solution and made to volume with water so that the final solution will contain 7% by volume of HNO_3. The uranium is extracted from an appropriate aliquot with ethyl acetate using aluminum nitrate as a salting-out agent. An aliquot of the ethyl acetate layer is then evaporated in a shallow platinum fluxing dish, 2 grams of a carbonate-fluoride flux are added and the mixture fluxed at 650°C to form a small disk. The percent fluorescence is then measured with a Galvanek-Morrison reflectance type fluorimeter, Model JA-2600, and the percent uranium calculated from a standard calibration curve.

Recalculation of the data

The amount of organic carbon was obtained by subtracting the carbonate carbon from the total carbon.

The quantity of carbonate mineral was obtained by multiplying the carbonate carbon value by 8.33, $\frac{\text{Mol. wgt. } CaCO_3}{\text{Mol. wgt. C}}$, for those samples which contained calcite and by 9.65, $\frac{FeCO_3}{C}$, for those samples which contained siderite.

The quantity of pyrite was calculated by subtracting the free iron from the total iron and multiplying the difference by 2.18, $\frac{FeS_2}{Fe}$.

The amount of iron oxides was obtained by multiplying the free iron value by 1.43, $\frac{Fe_2O_3}{2Fe}$. For samples that contained siderite, the appropriate amount of siderite iron was subtracted before multiplication.

Organic Material Analysis

Introduction

The hydrocarbons present in shales are of an extremely complex nature. As many as 65 organic compounds have been identified in the Colorado oil shale (Bureau of Mines, 1950). For this reason many workers investigating the organic portions of sedimentary rocks choose to determine only the amounts of the aromatic and aliphatic hydrocarbon present (Swain, F. M., 1956; Philippi, G. T., 1957; Smith, J. V., 1952, 1954; Kidwell, A. L. and Hunt, J. M., 1957). The total extraction of organic material is an extremely time-consuming procedure and the results are questionable, so a fraction of the total material is usually extracted and analyzed.

The solvents used for extraction are varied. Benzene, n-heptane, carbon disulfide, carbon tetrochloride, methanol, ethanol, acetone, and pyridine are often employed. Disopropyl and diethyl ether have also been used (Philippi, 1957).

The method of analysis of the extract has been improved in recent years. Early workers used a sulfuric acid separation (Brooks, B. I. and Humphery, I., 1948; Norris, J. F. and Joubut, J. M., 1927). Recently chromatographic methods have been favored (Swain, F. M., 1956; Smith, J. V., 1954; Forsman, J. P. and Hunt, J. M., 1957). In the chromatagrophic procedure commonly used, the extract is flushed through an alumina column with n-heptane, and then benzene. The portion of the extract obtained with the n-heptane is taken to be the aliphatic fraction and the material flushed by the benzene as the aromatic portion.

The addition of a Nuclear Magnetic Resonance Spectrometer to the equipment of the College of Chemistry and Physics of The Pennsylvania State University in the summer of 1957 enabled the writer to explore the possibility of quantitatively determining the amounts of aromatics and aliphatics present in shales using this instrument.

Nuclear magnetic resonance occurs when a substance containing free protons is exposed to crossed magnetic fields, one field being held steady and the other oscillating. When the strength of the former and the frequency of the latter are matched in a certain way, the nuclei are turned over in the steady field, and the energy is absorbed from the oscillating field. Another way of describing the effect is to say that the resonance occurs when the applied frequency is equal to the frequency of precession of the nuclei in the steady field. The principles of nuclear magnetic resonance are more completely described by Darrow (1953), Poules (1956), Andrew (1955), and Ingram (1955).

The applicability of this resonance phenomenon to the determination of the nature of the hydrocarbons (Williams, 1957) results from the occurrence of two relatively widely spaced lines in the spectra of substances such as toluene ($C_6H_5CH_3$). The hydrogen bonded to the aromatic type structure (ring structure) gives rise to a response line at 1000 cycles/sec whereas the hydrogen of the aliphatic structure (chain) gives rise to a peak at 1197 cycles/sec. The line shift caused by different compounds in either the aromatic or aliphatic groups is relatively small and, therefore, there is no overlap of lines between these groups. Since the intensity of a line is directly proportional to the quantity of hydrogen present, quantitative results may be obtained. In the case of toluene ($C_6H_5CH_3$) the ratio of the area under the aromatic line to that under the aliphatic line is 5:3.

Techniques

General

The procedure for the determination of organic compounds employed by the writer was largely controlled by limiting factors in Nuclear Magnetic Resonance Spectroscopy. Such factors determined the choice of solvent for extraction, the method of handling the extract and the minimum quantity of shale that could be analyzed.

The choice of solvents that could be used for extraction was limited to those that do not contain a free proton and have a favorable solubility parameter. The three common solvents that fulfill these requirements are carbon disulfide, carbon tetrachloride, and tetrachloroethylene. The boiling point of tetrachloroethylene (121.20°C) was found to be too high in that many of the extractable compounds boiled at lower temperatures and were lost. Carbon tetrachloride was also found to be impractical because of its tendency to combine with the extracted compounds causing them to congeal. The behavior of carbon disulfide was found to be favorable. Carbon disulfide, because of its low boiling point of 46.3°C, solubility parameter of 10.0, and dielectric constant of 2.6 proved to be a solvent that produced an adequate yield of soluble organic material.

The extremely volatile nature of CS_2, however, made handling difficult. A large volume (150-200 ml) of this solvent is needed for the extraction. This volume had to be reduced to 0.4 ml and transferred to and sealed in a length of 5 ml tubing. The CS_2 could not be allowed to evaporate and escape, because of its strong odor, toxic and explosive nature, and relatively high cost. To reduce the volume of the solvent without volatilizing the extracted organic matter contained in it, it was found necessary to build special controlled heating and vacuum apparatus.

The amount of shale necessary to produce a quantity of extract from which resonance peaks could be obtained was experimentally found to be five grams.

The quantity of toluene readily detectable in a CS_2 mixture was found to be 0.2% by volume.

Specific Details

The shales were ground to pass a 100 mesh screen and were thoroughly mixed by rotating the sealed sample containers end over end in a ball mill for 24 hours. Five grams of this ground shale was placed into a 80 x 33 mm., double-thickness, fat-free extraction thimble which was then placed in a Soxhlet extractor. Several glass beads were added to the 150 mls. of CS_2 used in the boiling flask. The CS_2 was boiled at a rate which allowed the extraction thimble chamber to be refilled every

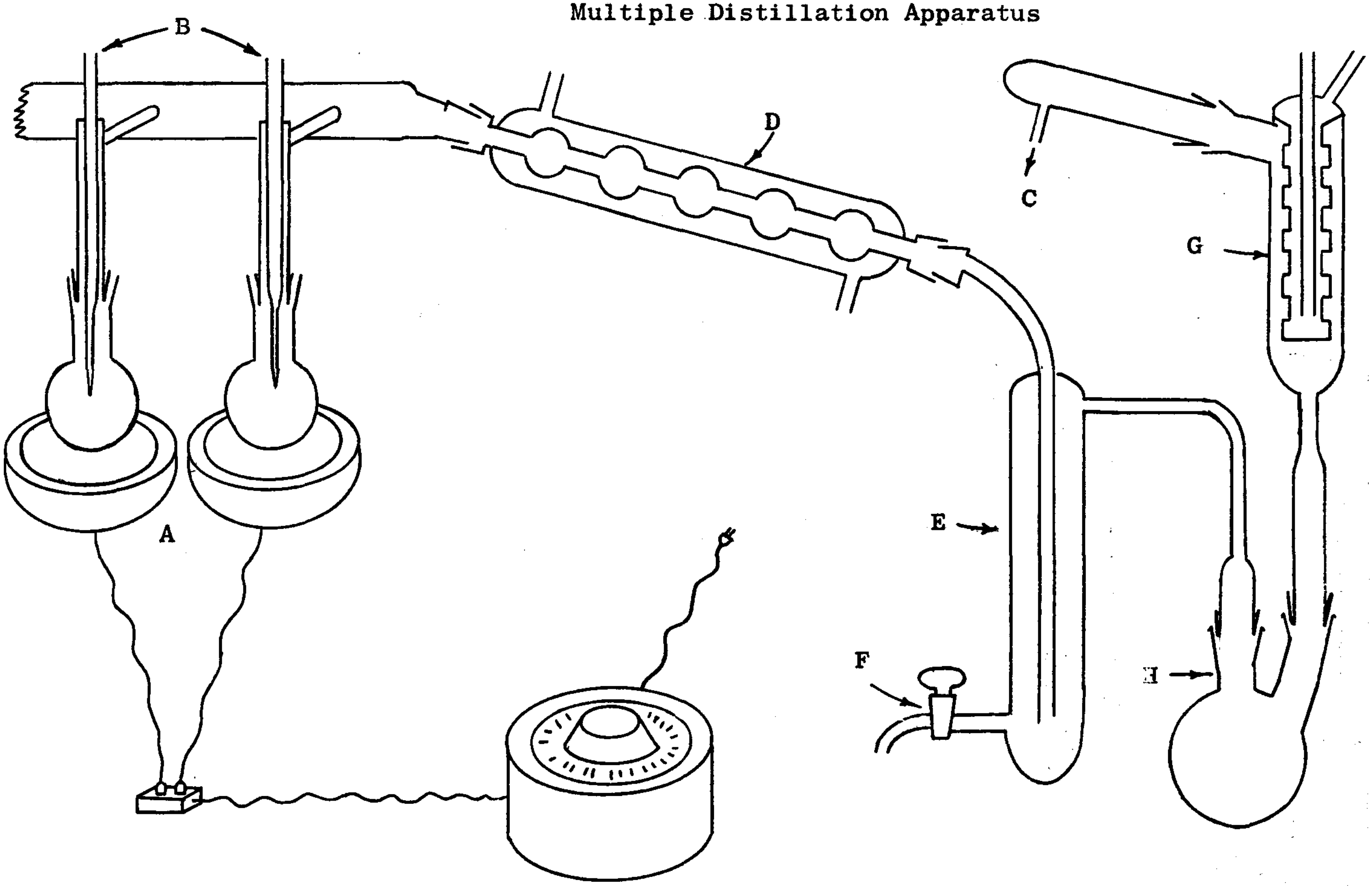
10 minutes. The extraction was found to be complete after 8 hours, but the process was continued for 11 hours to assure a complete and uniform extraction.

After the eleven hour extraction period the flask containing the solvent and the dissolved organic compounds was placed on the multiple distilling unit shown in figure 3. The solvent was slowly evaporated until only 15-20 ml. of solvent and organic material remained. The evaporation was hastened by gently warming the flask with a heating mantle (A), bubbling a small stream of nitrogen (B) through the solvent to prevent sample oxidation and to act as a carrier gas, and by a pressure reduction accomplished through the use of an aspirator (C). The condenser (D) and dry ice trap (E) (shown without dry ice jacket) condense the CS_2 which is drawn off through a valve (F) for re-use. The condenser at (G) serves as a safety measure and the trap (H) beneath it prevents water from contaminating the dry ice trap when the system is not in use.

Following the removal of all but 15-20 ml. of the CS_2, the extract is transferred to a small tube similar to a centrifuge tube but with a ground glass joint. The volume of the solvent is then further reduced under reduced pressure in the apparatus shown in figure 4. The solvent and extract (at A) are boiled down to a volume of 0.2 ml. The vacuum pump (B) and regulating valve (C) are used to maintain a partial vacuum of 30 mm. of mercury. The two traps (D) are required to catch the CS_2 which otherwise would enter the vacuum pump. The traps are submerged in Dewar flasks filled with liquid nitrogen. A nitrogen capillary (E) is

Figure 3

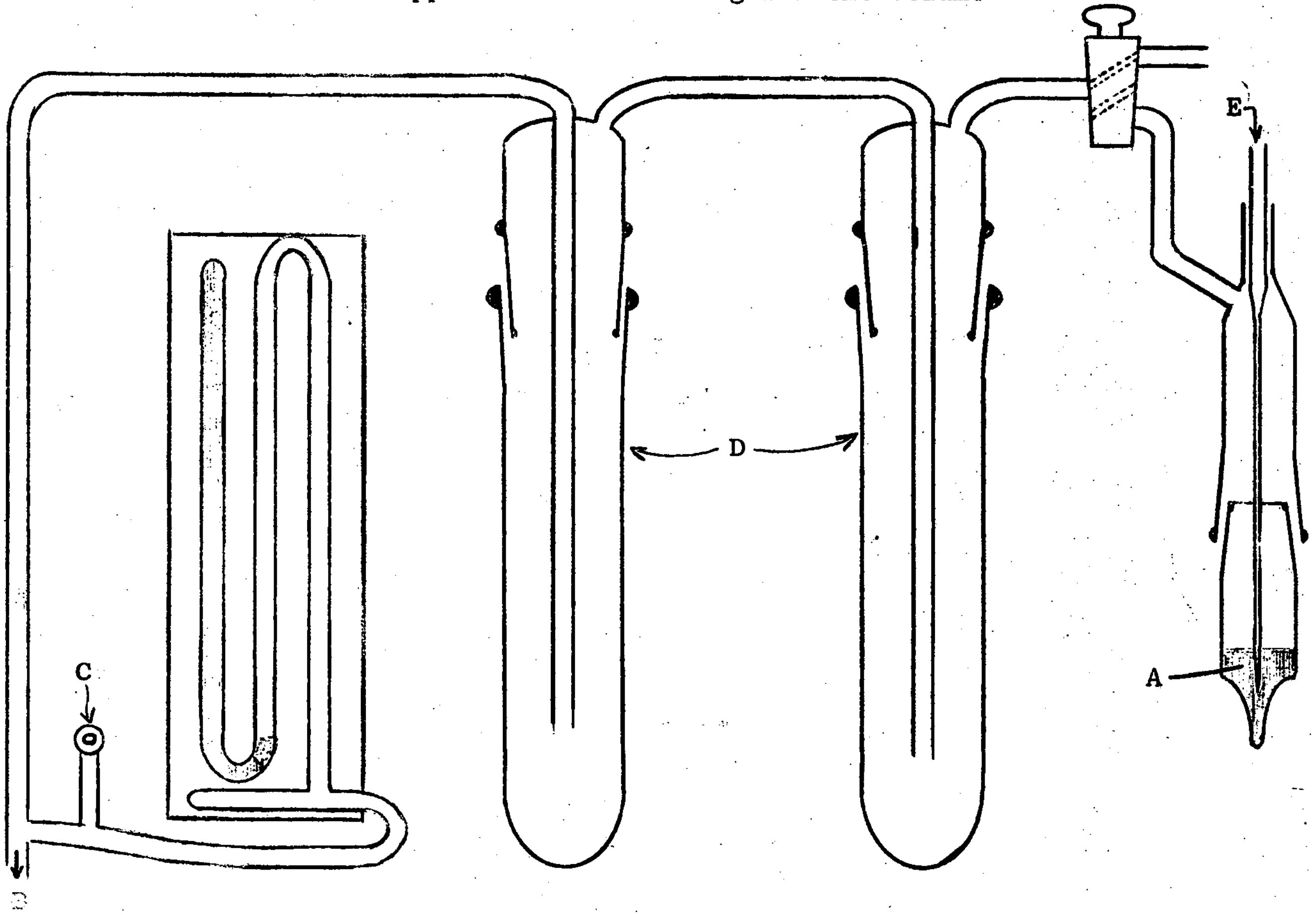
Multiple Distillation Apparatus



A. Flask and Heating Mantle, 2 of 6 units shown; B. Nitrogen capillary; C. To Aspirator; D. Condenser; E. Dry Ice Trap; F. Valve; G. Condenser; H. Trap.

Figure 4

Apparatus for Reducing Solvent Volume



A. Solvent and Extract; B. To vacuum pump; C. Regulating Valve; D. Liquid Nitrogen Traps; E. Nitrogen Capillary.

required to prevent bumping of the sample.

Upon obtaining a volume of approximately 0.2 ml., the extract is taken up into a 1 ml. hypodermic syringe. The sample tube is then washed twice with 0.1 ml. of CS_2. These washings are added to the extract and the entire 0.4 ml. transferred and sealed in a 5 ml. pyrex glass tube.

The sample is then placed in the radio probe of the Nuclear Magnetic Resonance Spectrometer and the aromatic and aliphatic peaks recorded. Examples of the spectrometer tracings are shown in figure 5. The areas under the peaks were found to be too small to be precisely measured. The peaks were, therefore, enlarged 4.6 times with an opaque projector and the areas measured with a compensating polar planimeter.

Precision and Translation of Results

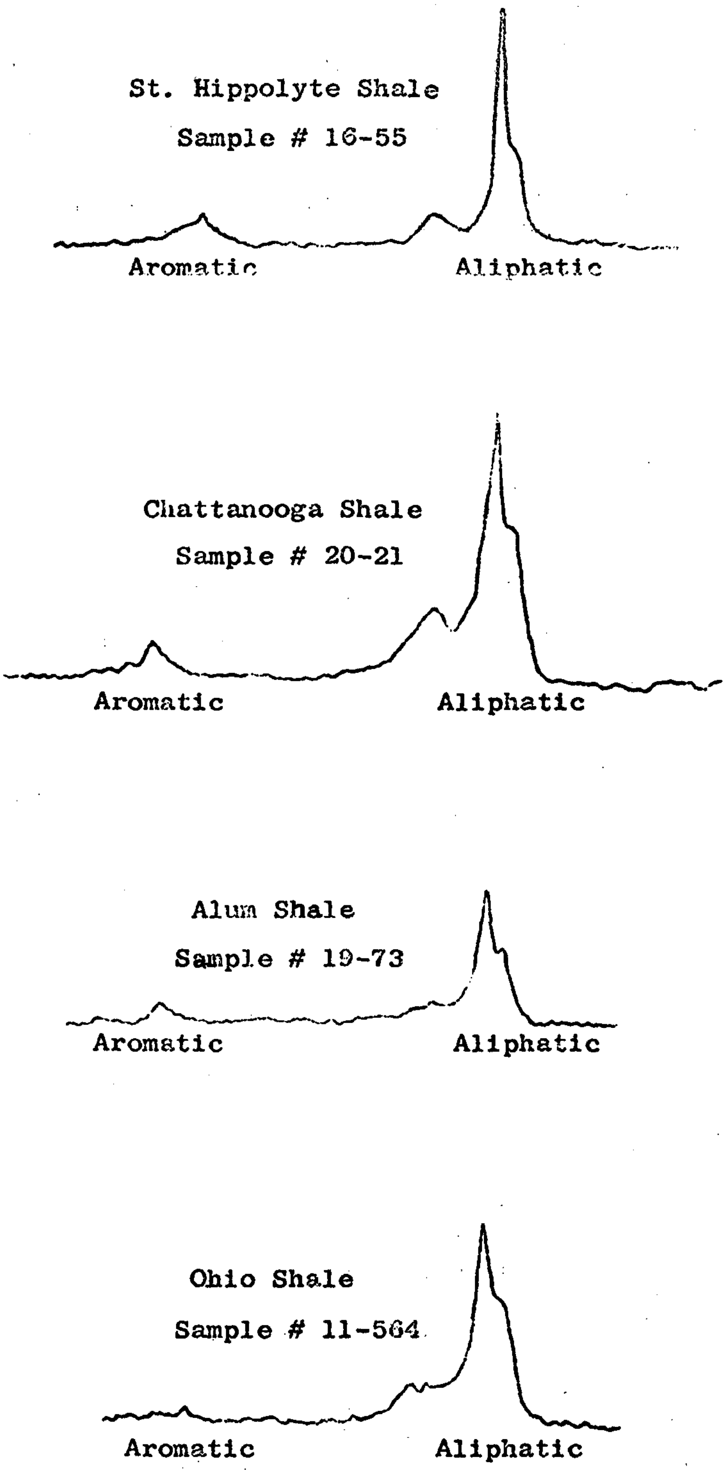
The precision of the organic determination discussed above must be considered in two separate discussions concerned with 1) the precision of the N. M. R. Spectrograph as it is being used in this work, and 2) the precision of the extraction procedure.

1) Since the operation of the spectrograph is somewhat subjective, rather than attempting to rigidly control the instrument to a narrow range of precision, the precision was determined for a conveniently wide operating range. The standard calibration curves and the precision limits (2 standard deviations of determined peak area) are shown in figure 6.

2) The precision of the extraction procedure was also empirically determined. Four replicate samples of each of the 4 shale formations

Figure 5

Nuclear Magnetic Resonance Spectrograms



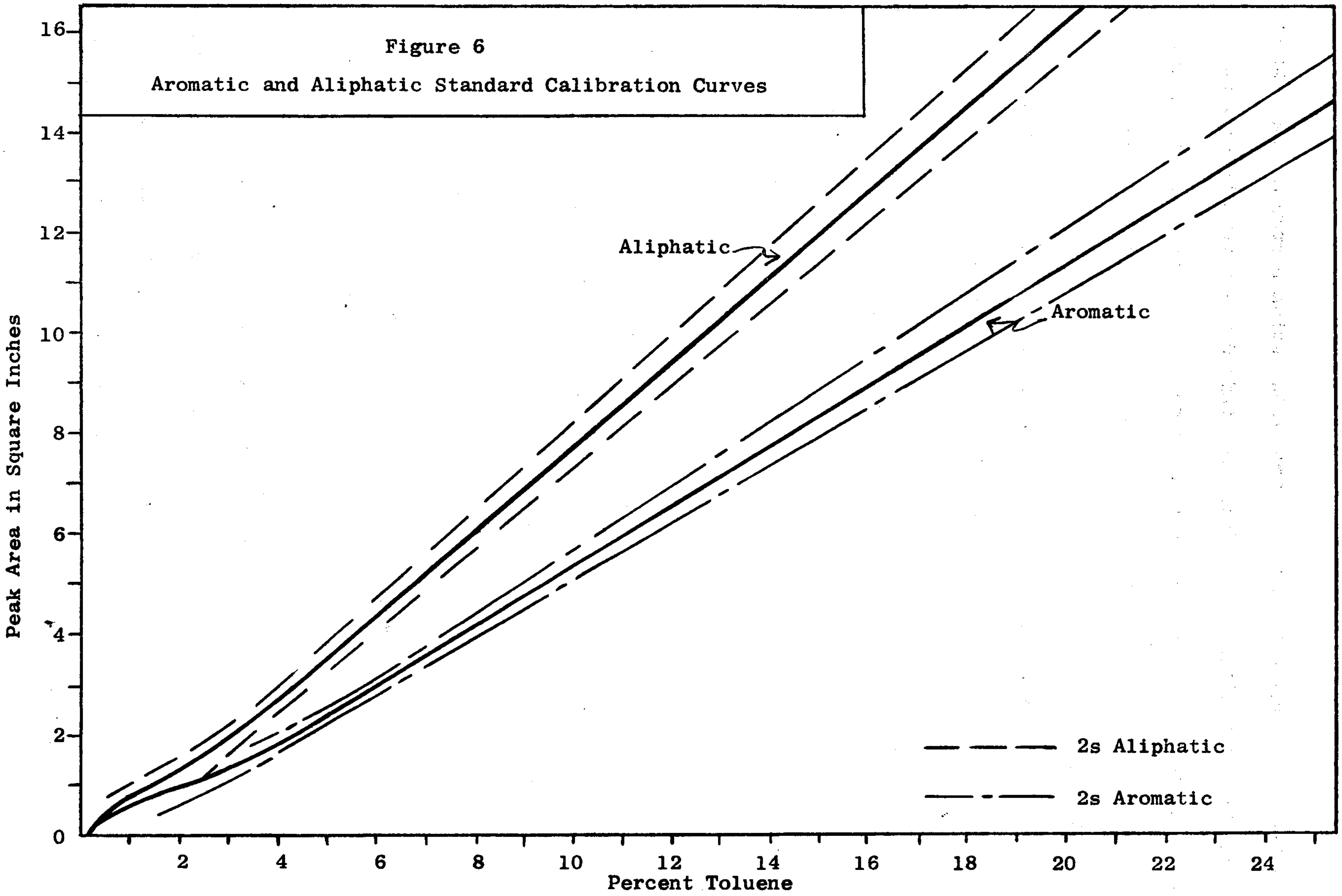


Figure 6

Aromatic and Aliphatic Standard Calibration Curves examined were analyzed to give a precision estimate over a range of the standard calibration curve. The two standard deviation limits were found to be ± 8% of the determined value. Since the molecular weights of the extracted compounds are not known, the results are expressed in equivalent percent toluene.

To define the lower limit of detectability of both the aromatic and aliphatic hydrogen, a fixed organic structure had to be assumed. A benzene ring was assumed for the aromatic material and a straight chain for the aliphatic compounds. The calculations may then be made on the toluene standard at the lower limit of detection (0.2% toluene by volume). The weight percent of the aromatic and aliphatic portions present in the 0.4 ml. of 0.2% solution of toluene was calculated back to the weight percent of a 5 gm. sample that they would represent. By employing these calculations, the lower limit of detectability of the aromatic compounds was found to be 9.8 ppm. and that of the aliphatic compounds found to be 2.3 ppm.

Silicate Mineral Analysis

Introduction

The qualitative and quantitative determination of the various silicate minerals in shales is best accomplished by x-ray diffraction analysis. The chemical compositions of the clay minerals are too variable to be quantitatively calculated from a chemical analysis of a mixture. Microscopic determination of mineralogic composition can be precisely made using the point count method (Chayes, 1946) but is unreliable for black shales (Strahl, et al, 1954, p. 53-54).

X-ray methods for the qualitative determination of the common silicate minerals of sedimentary rocks have been well established. Quantitative methods, however, are subject to question because of the variation in response of the clay minerals to x-radiation. Variations in degree of crystallinity, particle size, orientation, and composition of any given mineral affects its diffracting ability. There is no recognizable general solution to the problem, and therefore, the quantitative procedures commonly used are based primarily on operational definitions specific to each investigator.

The most common method employed consists of separating the less than 2 micron fraction of a sample by centrifugation and settling it on a glass slide (Grim, 1934). The x-ray diffractometer tracings are then obtained both before and after ethelyene glycol treatment. The abundance of kaolinite, mica (illite), chloritic clay minerals, and mixed-layer mineral are based on the relative intensities of the basal (001) sequences of the several clay mineral groups (Potter and Glass, 1958; Degens, et al, 1957). Since it is known that the distribution of diffraction intensity affects the intensity of (001) reflections (Bradley, 1954) many investigators (Weaver, 1958; Murray, 1953; Grim and Johns, 1953; Talvenheimo and White, 1952) correct the intensities of the (001) reflections by multiplication by appropriate factors.

The quantitative determination of quartz has been investigated by many writers (Alexander and Klug, 1948; Cervik, 1955; McCreery, 1949; Gross and Martin, 1949; Pollack, et al, 1954; Nagelschmidt, et al, 1952;

Gordon and Harris, 1955). The most serious sources of error in the quartz determination have been demonstrated to be variation in crystallinity and surface layers of amorphous or poorly crystalline material. Brindley and Udagawa (1957) have empirically shown that the x-ray intensity remains approximately constant throughout a particle size range from considerably greater than 10 microns to less than 1 micron, and that acid leaching strips the essentially amorphous surface layers of the quartz particles leaving a product that produces uniform x-ray intensity for a variety of quartz types.

Techniques

General Aspects

The primary objective of the quantitative silicate mineral analysis used in this study was to obtain data that was precise and consistent from shale to shale. The procedure employed was developed by the author after considering many of the limitations and sources of error in the methods of other workers. Of the major sources of error not evaluated by other workers, the effect of the variation in crystallinity on the x-ray intensity presented the most serious problem.

It was experimentally found that the variation in x-ray intensity from several different quartz, kaolinite, and illite samples could be reduced essentually to that of the x-ray machine variability by a combination of heating to 300°C, annealing, and acid leaching with dilute hydrochloric and nitric acids. In the treatment of shale samples, this process also had several other desirable effects. The heating, supplemented by a flow of oxygen, served to remove the organic material and oxidize the pyrite to an acid soluble oxide form. The acid leaching removed this soluble iron along with other minor elements and decomposed the carbonate material. As a result, the chemical composition of the samples was reduced essentially to silica and alumina, therefore, obviating the necessity of correcting for variation in the mass absorption coefficient. It also resulted in a marked decrease in the background scatter.

The consistency of the x-ray intensities obtained as a result of this sample treatment made it possible to use mixtures of standard reference samples of pure materials for calibration of standard curves.

A study of the stability of the x-ray machine and sample mixing and packing techniques demonstrated that the variability introduced by machine instability and slight variations in the sample preparation procedures did not appreciably effect the results. The x-ray intensities were, therefore, directly converted into a percentage value through the use of calibration curves instead of employing the customary internal standardization techniques.

It was decided to x-ray the bulk treated sample rather than the less than 2 micron fraction used by other workers because of the many obvious errors incurred when dealing with size fractions, and because the nature of the investigation called for an independent measure of each constituent rather than the relative proportions of components in a size fraction.

In using this analytical scheme, it was found that the analyzed amount of material accounted for as silicate components was considerably less than the quantity of chemically determined total silicates. This undetermined quantity was often considerably greater than could be accounted for by the unmeasured small amount of chlorite and feldspar known to be present in the samples. This portion of material unaccounted for is taken to be a rough measure of the amount of "x-ray amorphous" material present in each sample. The presence of this amorphous material was further indicated by the variation in x-ray background intensity. A large increase in background was noted in the region from 7° to 22° 2θ on the tracings of samples that contain a large quantity of amorphous material.

A primary consideration in this procedure is the rather severe effect the sample treatment has on the clay minerals. The heating and the acid leaching process destroys the chlorite minerals and collapses the 2:1 expandable, montmorillonite minerals to an approximate 10 Å spacing. These two compositional modifications were desirable in this work. Since the amount of chlorite present in the samples investigated was extremely small (generally $<2\%$) and approximately uniform, it was felt that a quantitative study of this mineral would not provide significant information. Since the (002) chlorite peak interferes with the (001) kaolinite peak, the removal of chlorite in the sample by this treatment allowed for a precise measure of the diffraction effect due to the kaolinite.

An almost similar situation exists for the montmorillonite minerals. Preliminary studies showed that only trace amounts of montmorillonite were present in a few samples and mixed-layer (10-14 Å) minerals in several others. The small amounts present, however, could not be quantitatively determined or isolated by any specific technique. For this reason, it was decided to group the montmorillonite, mixed-layer, and illite as the 2:1 layer lattice minerals. The heat treatment, in collapsing the montmorillonites led to a single integrated measurement of the 2:1 layer minerals at approximately 10 Å.

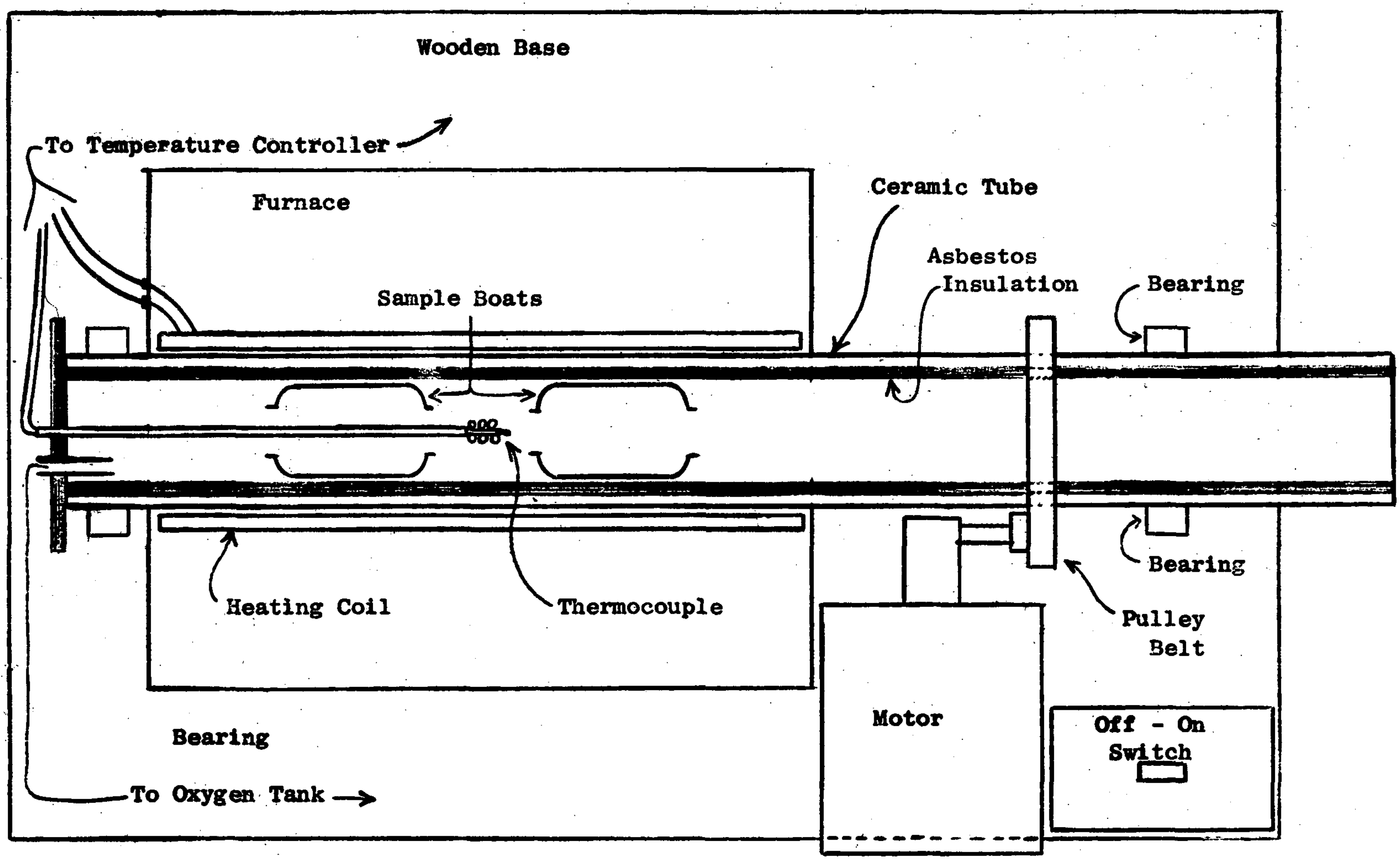
The possible interference of the (003) illite reflection in the (101) quartz reflection was also investigated and shown to be negligible.

Specific Details

The insoluble portion of the shale sample remaining in the extraction thimble after the organic extraction described in the previous section, was transferred to a pyrex glass sample boat and placed in the specially constructed furnace shown in figure 7. The sample boat was placed in the asbestos paper-lined ceramic tube which was rotated at a speed of 10 rpm. to insure uniform heating and cooling of the sample. The rotation of the ceramic tube was accomplished through the use of a 1/5 hp. motor, a gear reduction unit, and a V belt. The samples were heated at a rate of 200°C per hour until a temperature of 300°C was reached. This temperature was held for one hour and then the furnace was cooled at the rate of 200°C per hour to room temperature. The temperature was controlled within ± 5°C with a Micromax (Leeds and Northrop) temperature controller. A stream of oxygen wet by bubbling through a water bath was passed over the samples during the entire operation

Figure 7

Sample Furnace



at the rate of 3 cubic feet per minute.

After cooling, the sample was transferred into a 400 ml. beaker and 200 mls. of a 1:1 mixture of 1:10 hydrochloric acid and 1:10 nitric acid were added. The sample was digested at 85°C for 24 hours, filtered, washed, and dried.

The sample was then mixed by gentle grinding in a mortar and a portion of it was packed in an aluminum x-ray slide containing a 9/16 inch diameter powder well. The packing was accomplished by first gently placing the sample in the well and then pressing firmly with a large rubber stopper.

The packed sample was run on a high angle Norelco recording spectrogoniometer using Cu Kα radiation.

The calibration curves used to convert the recorded x-ray intensity into equivalent mineral percent are given in figures 8 through 10. The $2s_y$* precision limits are also given in these figures.

The differences between the chemically determined total silicates and the sum of the quartz, kaolinite, and illite was calculated to be the amount of x-ray amorphous material. Each of the portions of the total silicate fraction was then multiplied by the percent total silicates and recorded as the percent of the total sample.

Spectrochemical Analysis

Introduction

The quantitative determination of molybdenum and manganese in black shales is, at present, best accomplished by spectrographic methods. The

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* Standard error of estimate of linear portion of curve; 2 standard deviations of determined portions for curvilinear portions.

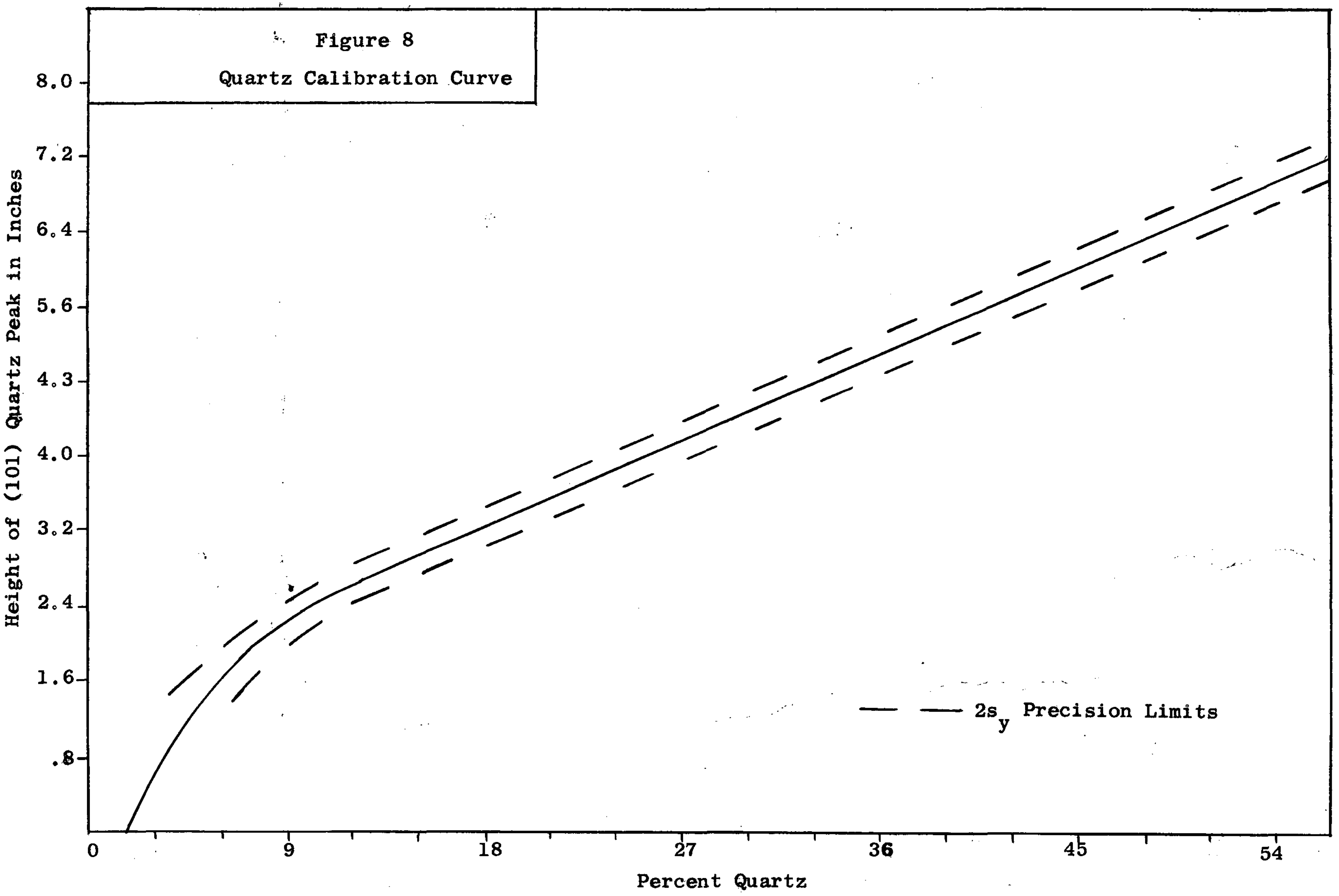


Figure 8

Quartz Calibration Curve

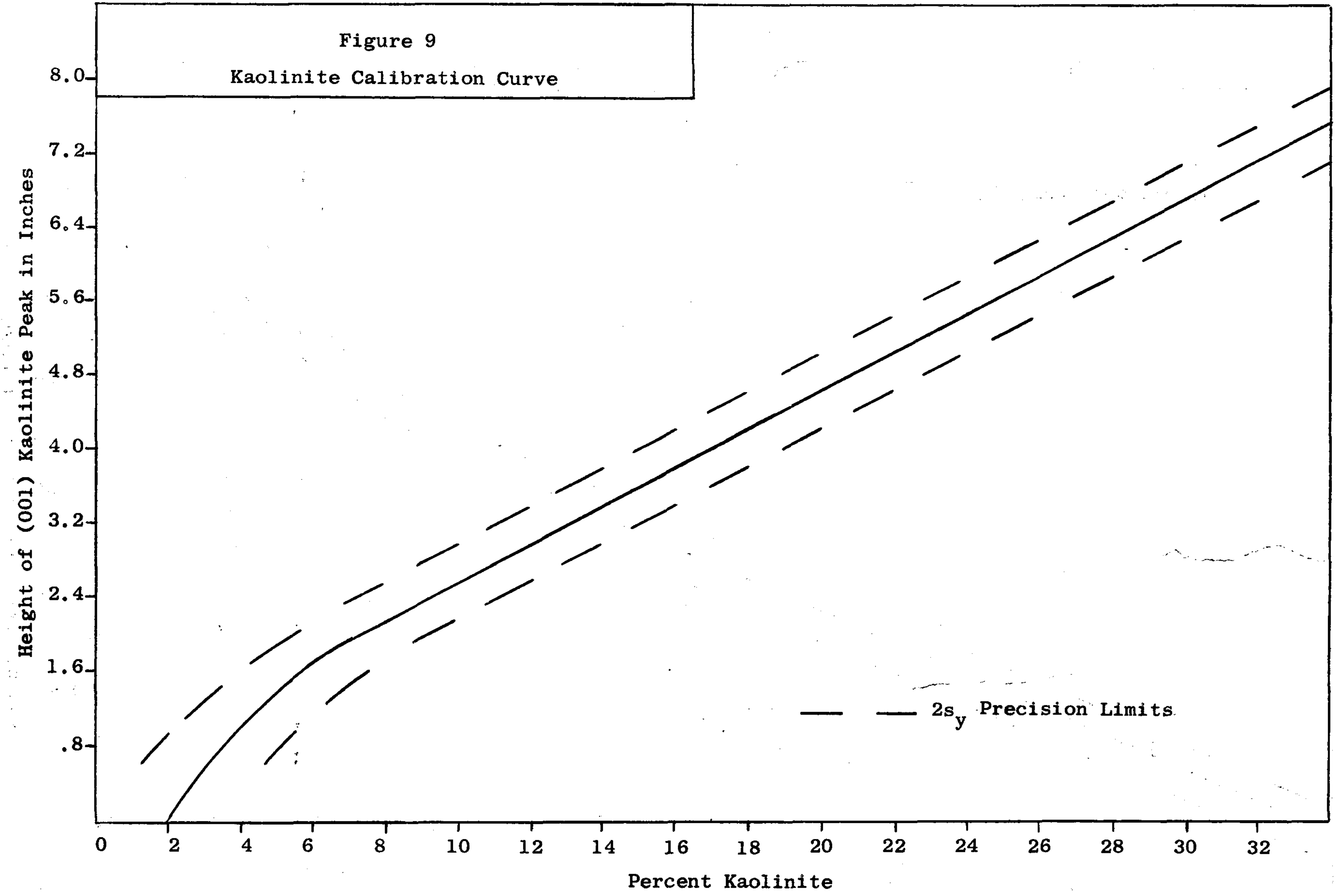


Figure 9

Kaolinite Calibration Curve

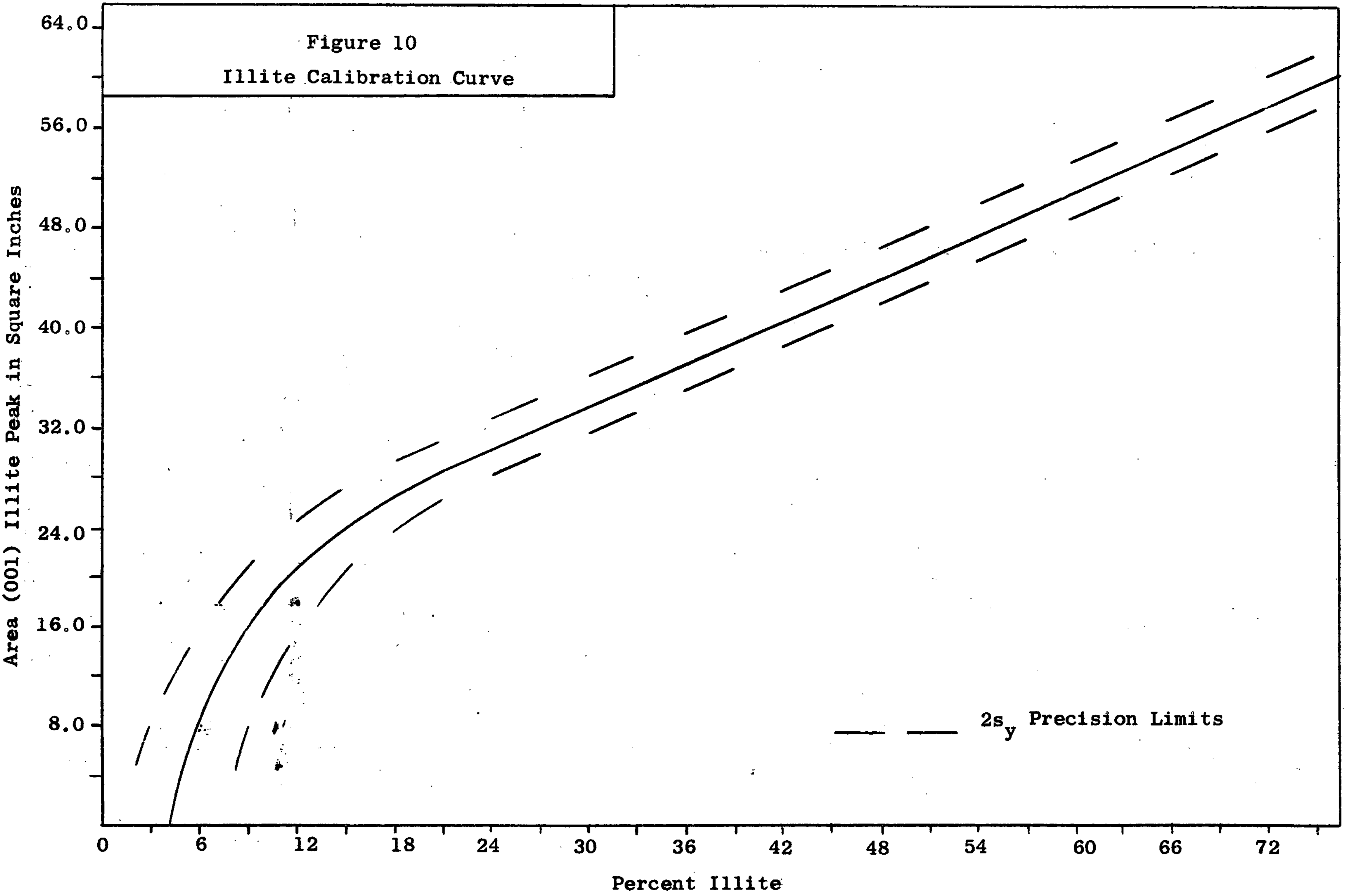


Figure 10

Illite Calibration Curve

wet chemical, and x-ray fluorescence methods are precise and accurate for minor quantities of these elements (O'Neil, 1958) but fail to produce acceptable results for the trace quantities that are present in shales (O'Neil, 1958a). The precision and accuracy of the colorimetric determinations (Willard and Greathouse, 1917; Will and Yoe, 1953) are greater than those of the spectrographic method but the preparation procedures are extremely time consuming and therefore prohibitive for the analysis of a large number of samples.

In the quantitative method of spectrochemical analysis most commonly employed in the investigations of shales, a given weight of sample is mixed with a given amount of a buffer and completely volatilized in a D.C. arc (Degens, et al., 1957; Duey, 1957; O'Neil, 1956). The quantitative values are determined by a direct relationship between element concentration and recorded transmittance from photographic plates. This general procedure is often varied to include the use of internal standards (Rushton and Nichols, 1957; Ahrens, 1950; Heggen and Strock, 1953). By working in terms of ratios provided through the use of internal standards, many of the errors due to variations inherent in spectrographic analysis, such as those connected with sample preparation, excitation, illumination, exposure time, photographic development, and line measurement conditions are minimized.

Mutual standard methods (Dennen and Fowler, 1955; Couliette, 1943; Churchill and Russell, 1945) make use of a self contained variable internal standard (Mitchell and Scott, 1957) and eliminate the time and error involved in the addition of a known standard to the unknown mateial to be analyzed. These methods are quite precise when the complete elemental analysis is performed but subject to large errors in shales where as much as 20% of the material cannot be measured spectrographically (Short, 1958).

The spark solution method of spectrochemical analysis (Mathis, 1953; Feldman, 1950; Yoe and Koeh, 1957; Fry, 1957) is becomming increasingly popular and offers several advantages over the arc methods, such as: the elimination of mixing and weighing problems through the use of solutions, the elimination of the interferences of the cyanogen band, the ease with which a portion of the solution may be totally volatilized and the uniformity of the excitation conditions with a minimum of operator control. Disadvantages include a decrease in sensitivity (which can be compensated for by an increase in solution concentration) and the chemical preparation necessary to put the sample into solution. A more complete discussion of spectrochemical methods may be found in Ahrens (1950).

Techniques

General Aspects

The nature of the investigation conducted by the writer made it feasible to combine the spark solution method and a modified form of the mutual standard method. Since only the elements manganese and molybdenum were sought, the acid extract, obtained as a by-product of the sample preparation for the x-ray analysis, could be used. The variable internal standard, iron, quantitatively determined by x-ray fluorescence, was also quantitatively present in the acid extract.

The ratios between the iron and molybdenum and iron and manganese were determined spectrographically. This process minimized the inherent spectrographic errors to a point where the intensity ratio could be determined with an error of less than ± 2% (2s*) of the determined value, in contrast to the normally expected spectrographic error of 10-15%.

In order to determine the actual amount of molybdenum or manganese present in the samples from the ratio data, it was necessary to construct a series or "nest" of calibration curves. Through the use of this nest of curves, each individual curve representing a different known iron concentration, the amount of Mo or Mn was determined from its ratio to iron $\left(\frac{I_0\text{Mo}}{I_0\text{Fe}} \text{ or } \frac{I_0\text{Mn}}{I_0\text{Fe}} \right)$.

The concentrations of the solutions were controlled by bringing them to a constant volume in order to keep within the range of maximum spectrographic sensitivity and precision.

Specific Details

The acid extract obtained as a result of the silicate analysis sample treatment process was brought to 50 ml. and a 1 ml. aliquot was transferred to a 1 ml. porcelain boat and volatilized on the surface of a rotating carbon disc. The following spectrographic conditions were maintained throughout this study.

Electrodes. All electrodes were made of high purity grade carbon. The counter electrode (cathode) was 3/16" in diameter,

* 2s = two standard deviations.

1-1/2" in length and sharpened to a point. The lower electrode (anode) was a 1/2" in diameter disc, 1/8" thick, mounted on motor driven axle turning at 10 rpm. New electrodes were used for each sample.

Spectrograph. A 21-foot Jarrell-Ash Wadsworth grating spectrograph, Model JA-70 15 m. was used. The grating has a ruled area of approximately 5-3/8 inches by 2-1/4 inches, ruled with 15,000 lines per inch with a reciprocal linear dispersion of 5.0 angstroms per mm.

Recording Equipment. Spectra in the spectral region from 2325 Å to 3500 Å were recorded on Eastman Spectrum Analysis No. 1 emulsion plates, 4 inches by 10 inches.

Excitation. The samples were volatilized in a 2KVA spark at 0.021 μF capacitance and .045 millihenries inductance.

Exposure. The plate exposure time was 30 seconds. Slit width was set at 40 microns and slit height at 1.5 mm.

Photographic Processing. The emulsion plates were developed for 5 minutes in a solution of Kodak Developer D-19, rinsed in water, and left for 12 minutes in a fixing solution prepared from Kodafix. The developing and fixing was done in a rocking-type tray holder in which the solutions were automatically maintained at a temperature of 20°C. After fixing, the plates were washed for 20 minutes in running water, rinsed in a Photoflo solution, and dried for 4 minutes.

Comparator-Densitometer. An Applied Research Laboratories Comparator with a screen magnification of 20 was used to locate the spectral lines of the elements on the analysis plates and to measure the density of the lines.

Approximately 30 exposures were made on each plate in addition to a step-sector iron arc exposure (for emulsion calibration).

The density of two spectral lines was measured for both molybdenum and manganese to insure against aberrant values and to extend the analytic range. To remove the effects of variable emulsion sensitivity and fogging, the density of an iron line in close proximity to each molybdenum and manganese line was also measured. The lines used are given below:

Element	Line
Mo	2816.154 Å
Fe	2823.276
Mo	2890.994
Fe	2885.928
Mn	2576.101
Fe	2569.764
Mn	3460.328
Fe	3445.151

Using a separate emulsion calibration curve for each pair of lines (Mn-Fe or Mo-Fe) on each plate, the intensities (I_o) of the lines were determined. The amount of Mn or Mo was then obtained by calculating the ratios of the intensities, $\frac{I_o\text{Mo}}{I_o\text{Fe}}$ or $\frac{I_o\text{Mn}}{I_o\text{Fe}}$, for each pair of lines and reading the value from the nest of curves, figures 11 and 12.

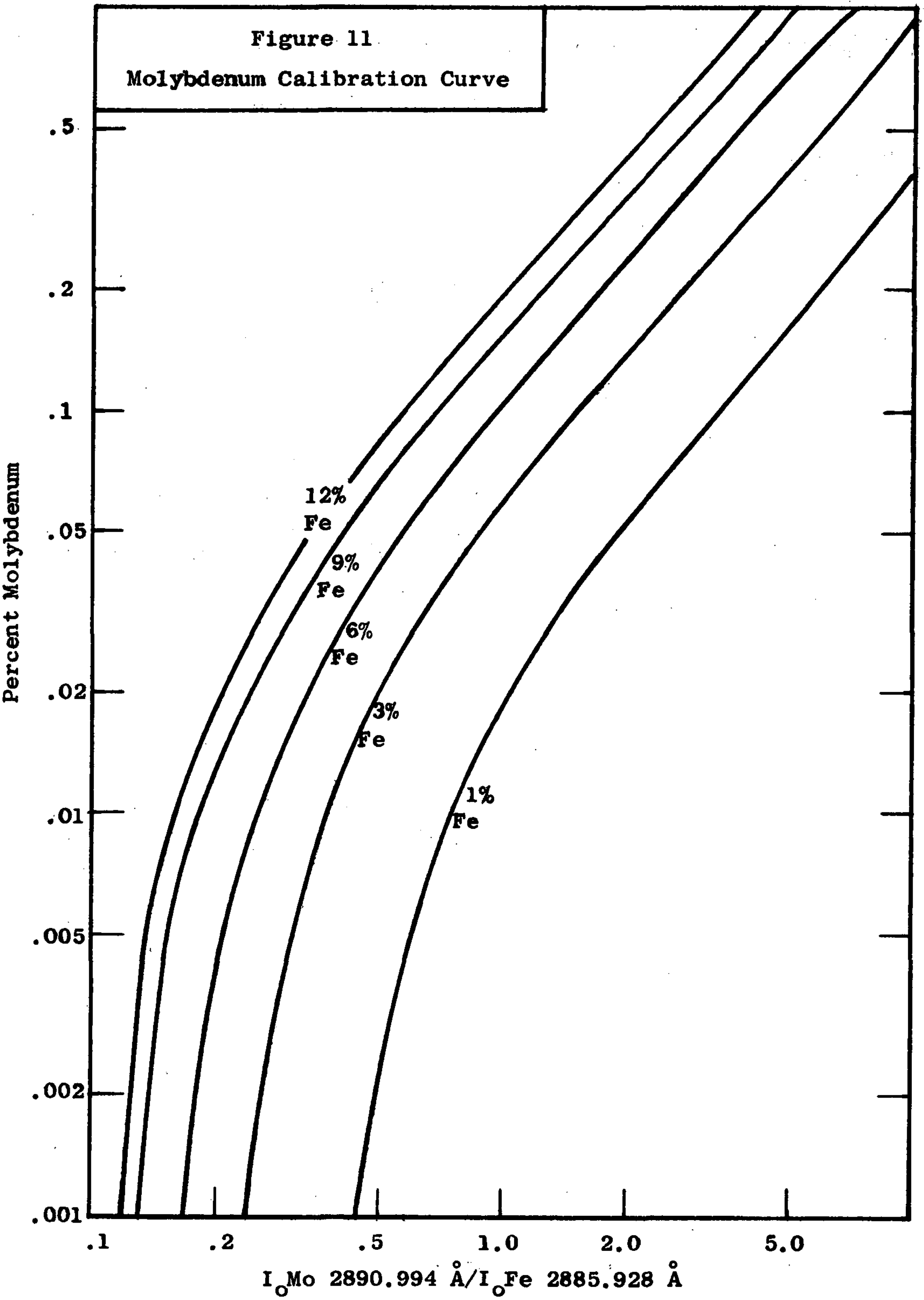


Figure 11

Molybdenum Calibration Curve

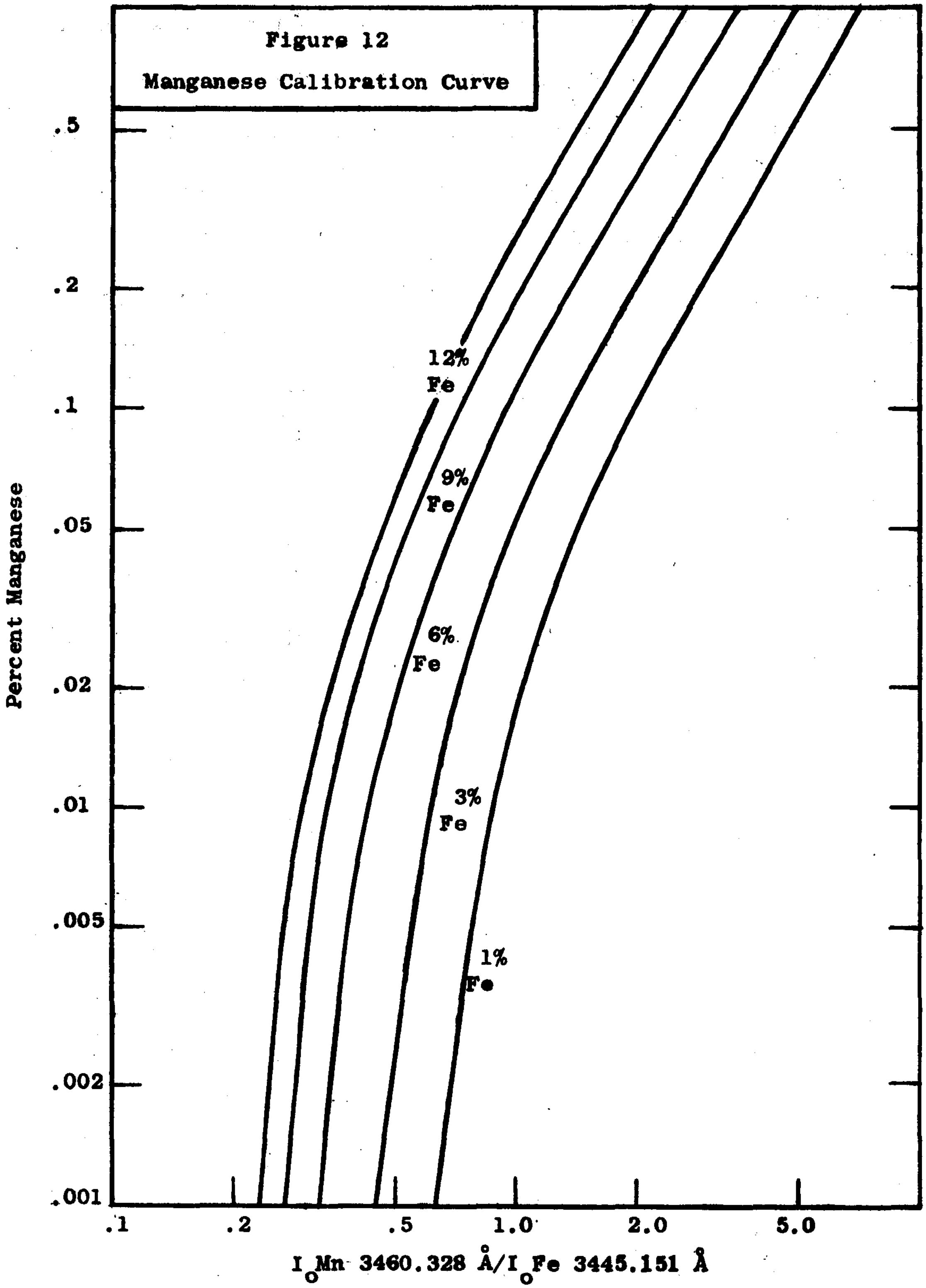


Figure 12

Manganese Calibration Curve

The nests of curves in these two figures are not complete and are given only as illustrations of their form. The curves used were actually plotted at 1% iron intervals rather than the 3% intervals shown. Only the curves used for higher concentrations are illustrated. Those used for values of less than .010% have been omitted.

The precision of the entire spectrochemical procedure as calculated from the analysis of replicate samples was ± 5% (2s) of the determined value.

Quartz Grain Size

Introduction

Many methods have been developed for the measurement of grain size. Loose grain methods (Krumbein and Pettijohn, 1938; Pye, 1943; Hulbe, 1957) are not applicable to black shale research because of the difficulty of disaggregating the rock without altering the size of the quartz particles. The thin section methods (Chayes, 1949 and 1950; Griffiths, 1952; Rosenfeld, 1954) are applicable but the generally accepted practices cannot be employed because of the fine-grained nature of the shales.

A method used in the study of shales must be one in which the amount of fine-grained material, the material too small to be measured under the light microscope, does not effect the stability of the measurements. The generally accepted grain size distribution statistical techniques (Krumbein and Pettijohn, 1938; Krumbein, 1938; Griffiths, 1955) cannot be used because the measures of central tendency depend on measurements of the finer as well as the coarser sizes.

Quartz grain size measurements in shales are also affected by compositional variations. The lower size limit to which a particle can be detected depends partially upon the amount of organic material, clay, and pyrite in the rock. However, a stable estimate of the coarsest quartz grains present in thin sections of shale can be made and, therefore, these grains can be used to determine the maximum quartz grain size.

Techniques

General Aspects

The quartz grains in the shales under investigation ranged in size from approximately 100 microns to a value well below the theoretical limit of resolution of the light microscope (0.2μ). It was experimentally found, that stable size measurements could be obtained on material that was larger than 2μ in diameter. However, the difficulty and time involved in making measurements on large numbers of $>2\mu$ grains in fine-grained shales renders the technique impractical for the study of a large number of thin sections.

The technique adopted by the writer proved to be rapid and the results were found to be stable. The number of grains measured in each thin section was limited to ten by measuring only the largest grain in each of ten traverses. The average value was then taken as the average maximum quartz grain size.

Since in black shales the identification of even the largest quartz grains may be inconsistent, an operational definition of quartz was employed. By this definition, quartz included all well defined quartz and untwinned feldspar grains (Strahl, et al. 1954, p. 33).

Specific Details

A Bausch and Lomb combination petrographic and metallographic microscope equipped with a 100X oil immersion objective, a 10X ocular containing a graduated scale, and a mechanical stage was used. The magnification of the optical system (with immersion oil) was 1,250 diameters.

The thin sections were cut perpendicular to the bedding, and ground to a thickness of approximately .0010 mm. Cover glasses were not used. The sections were placed in the mechanical stage, covered with immersion oil and traversed in a direction parallel to the bedding. Any grain lying wholly or partly in the central 1/3 of the microscope field was included in the traverse. The traverse length was fixed at 20 mm. The grain with the longest apparent axis was taken as the largest grain in each traverse. Ten traverses were run and the average size of the 10 grains recorded as the average maximum quartz grain size.

METHODS OF DATA ANALYSIS

Introduction

The determination of the relationships between variables is best accomplished by statistical methods. The simple correlation coefficient is used to determine the relationship between two variables, and several types of multivariate analysis may be used to determine the relationships between groups of variables.

Simple correlation statistics have been effectively employed in geological research (Correns, 1948; Strahl, et al, 1954 and 1955; Bates, et al, 1956; O'Neil, 1956; Duey, 1957; Dolsen, 1957) during the last decade but the multivariate approach is relatively new to the geological field. Discriminatory analysis was found to be effective in the differentiation of sediments on the basis of variation in composition and texture (Emery and Griffiths, 1954; Hulbe, 1957; Shadle, 1957) and the application of this method of analysis to petroleum geology is discussed by Griffiths (1958).

A second type of multivariate statistical analysis, multiple regression and correlation analysis, has been shown by Bates and the writer (1958) and by Duey (1957) to be effective in showing the relationship of a minor constituent to the composition of a sediment.

A third type of multivariate analysis, factor analysis, was employed by Bowden (1954) to show the interrelationships of several rock constituents, but the effectiveness of his analysis was severely limited by the lack of an adequate number of analyzed samples and constituents. The factor analysis method is used by the writer in this study as a means of providing information on the interrelationships of shale constituents and their relationship to environmental factors.

Simple Correlation

In order to determine the relationship or association of one measured component with another, the Pearson product-moment correlation coefficient (r) was used. This statistic is also often referred to as the zero order or bivariate correlation coefficient and is defined as: $r = \frac{\Sigma (x-\bar{x})\ (y-\bar{y})}{N\sigma x \sigma y}$ (Snedecor, 1946), where $\bar{x}$ is the mean of all the x values and $\bar{y}$ the mean of all the y values, σx and σy are the standard deviations of all the x values and all the y values, and N is the number of samples. The correlation coefficient, r, can have values from -1 through 0 to +1. When r = -1 there is perfect negative correlation and an increasing x is associated with decreasing y. When r = +1 there is perfect positive correlation and an increasing x is associated with an increasing y. When r = 0 there is no correlation between x and y.

The significance of a correlation coefficient is determined by the probability of occurrence of a larger coefficient from a random sample drawn from a population without correlation ($\rho = 0$). When the r value is significant at the 0.05 level it means that the odds are 1 in 20 against obtaining a correlation coefficient this great by chance alone. When the r value is significant at the 0.01 level it means that the odds are 1 in 100.

The coefficient of determination, the square of the correlation coefficient expressed in percent, is a measure of the degree of association or the amount of variation common to both factors.

Factor Analysis

The applications of factor analysis up to the present time have been chiefly in the field of psychology, because the methods were invented by psychologists for dealing with certain of their problems. Factor analysis has been described by Holzinger and Harman (1951, p. 3) as:

> "... a branch of statistical theory concerned with the resolution of a set of descriptive variables in terms of a small number of categories or factors. This resolution is accomplished by the analysis of the intercorrelations of the variables. A satisfactory solution will yield factors which will convey all the essential information of the original set of variables. The chief aim is thus to obtain scientific parsimony or economy of description."

Several types of factorial solutions have been developed, and many of them are highly subjective. Perhaps the most mathematically rigid, and therefore, least subjective method, is the principal axes solution (also called principal components or principal-factor method) developed by Hotelling (1936). Since the calculation procedures are too lengthy and complex to be considered within the scope of this work, the reader is referred to one of the following texts for an adequate description: Holzinger and Harman (1951), Fruchter (1954, and Thurstone (1947). A brief discussion of the principles and objectives of the method is, however, necessary at this time.

To study the relationship between two variables, one may plot data on a two dimensional graph and then discuss its configuration in terms of the two orthogonal axes. Similarly, three variables may be discussed in terms of three orthogonal axes. For four or more axes the data cannot be physically plotted and its configuration must be visualized in hyperspace of four or more dimensions. In an n-dimensional configuration, any one variable must be explained in terms of all n dimensions. The object of factor analysis is to reduce the number of dimensions and yet retain the information contained in the n dimensions.

To accomplish this, a line or axis is mathematically located by a method of successive approximation through the longest axis of the n-dimensional configuration (n = 15 in this study). The ability of this line (factor) to explain the spatial distribution of each variable is calculated as a factor loading for each variable. The factor loadings may be thought of as correlation coefficients for the factor and the variables. The variation in the data, unexplained by the factor (or line), is computed as a residual correlation matrix and a second factor is then computed (the longest axis of the configuration orthogonal to the first axis). The factor loadings and the residual correlation matrix are again obtained and a third factor is computed. The process is continued until the residual correlations no longer contain significant interrelationships (the residual correlation coefficients do not differ significantly from zero).

The factors obtained by this method are uncorrelated and contain all the information of the original correlation matrix.

The importance of each factor relative to the remaining factors can be determined and is expressed as percent contribution. The percent contribution of a given factor may be defined as:

$$\text{Percent Contribution} = \frac{\sum_{1}^{n} x^2}{\sum_{1}^{m} \sum_{1}^{n} x^2} \cdot 100,$$

where x is the factor loading for a variable, n is the number of variables, and m is the number of factors.

The mathematically obtained factors are not directly definable in terms of the underlying factors of the variables. An identification of the factors is made through the factor loadings; that is, the identity of a factor is obtained from the variables that have high factor loadings on that factor.

Many factor analysts consider the principal axes solution to be an incomplete solution to a factor analysis problem and complete their analyses by rotating the factors (or axes) to a desired solution. The writer found this process too subjective for this study in that several solutions could be obtained for a given set of factors.

The factor analysis computations, as well as the correlation computations, were carried out with the aid of PENNSTAC, a digital computor in the Department of Electrical Engineering, The Pennsylvania State University.

PRESENTATION AND ANALYSIS OF THE DATA

INTRODUCTION

The data obtained by the methods discussed in previous sections are given in the Appendix. The analysis is limited to those variables which measured specific components. The composite measures of total carbon and total iron are therefore deleted. The measure of total silicates is, however, retained because of the possibility of this measure representing the quantity of detrital material present in a sample. The variables employed in the statistical analysis and the means and standard deviations for each shale are given in table I. The means and standard deviations are tabulated to facilitate the discussion of the analysis of the data.

Since it was not an objective of this study, precise testing of the data to determine significant differences between the shales was not undertaken.

The analysis of the data is presented and discussed in two phases; 1) the bivariate relationships of the variables and 2) the multivariate relationships. The mathematical limitations of the analyses affected by the nature of the data are similarly discussed.

BIVARIATE RELATIONSHIPS

General

The bivariate relationships of the variables were determined by calculating the simple correlation coefficients (r) for the variables

Table I

Means and Standard Deviations

Means

SHALE	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicate	Quartz	Kaolinite	Illite
Chattanooga	.82%	10.79%	.67%	8.72%	70.0%	27.0%	3.2%	23.9%
Ohio	.53	2.01	2.07	4.35	79.2	22.9	7.0	41.3
St. Hippolyte	2.34	9.23	5.15	1.66	49.0	6.6	12.4	13.6
Alum	.23	16.96	.72	11.14	57.8	15.5	3.9	11.6
Total	.92	10.23	1.77	7.10	65.0	19.8	5.8	22.4

Standard Deviation

SHALE	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicate	Quartz	Kaolinite	Illite
Chattanooga	1.56%	4.37%	.15%	3.55%	7.5%	8.2%	.7%	10.6%
Ohio	.88	2.06	.27	1.40	3.5	4.6	2.3	11.1
St. Hippolyte	3.69	5.24	4.68	1.11	13.8	9.1	7.1	9.2
Alum	.39	2.67	.15	1.98	2.8	4.6	.9	7.3
Total	2.06	6.19	2.68	4.27	13.1	10.5	4.8	14.3

Table I
(continued)

Means

SHALE	Amorphous	Aromatic	Aliphatic	Uranium	Molybdenum	Manganese	Quartz Grain Size
Chattanooga	16.3%	.43%	11.59%	.0053%	.024%	.036%	20.8µ
Ohio	8.3	.08	3.69	.0008	.025	.036	15.8
St. Hippolyte	16.4	.18	2.52	.1259	.075	.097	22.2
Alum	26.8	.18	4.12	.0188	.018	.028	11.4
Total	17.2	.26	6.73	.0304	.033	.045	17.9

Standard Deviation

SHALE	Amorphous	Aromatic	Aliphatic	Uranium	Molybdenum	Manganese	Quartz Grain Size
Chattanooga	9.1%	.37%	5.64%	.0020%	.025%	.026%	9.5µ
Ohio	9.9	.12	3.13	.0006	.007	.020	9.1
St. Hippolyte	7.5	.23	2.08	.3170	.058	.090	25.1
Alum	8.6	.13	1.68	.0093	.008	.016	1.5
Total	10.6	.30	5.67	.1461	.036	.048	13.7

taken in pairs. Since only linear relationships were sought, variables which might give rise to curvilinear bivariate distributions were analyzed using both the experimentally determined values and log transformed values. The correlation coefficients were determined for both the determined values and the logarithms of carbonate, uranium, molybdenum, and manganese and for both the determined and Phi ($-\log_2 \cdot$diameter) grain size. Only uranium showed an increase in linearity (as reflected by higher correlation coefficients) when a log transform was employed.

The correlation coefficients obtained for each of the shales and for the four shales combined are given in tables II through VI.

Several of the bivariate relationships were found to be consistent both within shales and between the shales. This consistency may be noted, for example, between molybdenum and manganese. A high positive correlation exists between these two variables in each shale and for the four shales combined. The bivariate distribution is graphically illustrated in figure 13. Similar relationships may be found in the distribution of organic carbon - total silicates and organic carbon - pyrite (figure 14).

In general, however, consistent relationships between all shales were not found. This lack of consistency is in part due to differences that exist between shales and partly due to the nature of the data and the sampling procedure. The inconsistency due to differences between shales can be noticed in the relationship of illite to amorphous silicates. In figure 15, a plot of percent illite against percent amorphous material, it can be seen that the St. Hippolyte shale differs

Table II

Simple Correlation Coefficients,

Chattanooga Shale

	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicate	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size
CO_2	1.0000	-.5531	-.3948	-.2342	.1353	.5799	-.1229	-.4522	.1193	-.2635	-.4663	-.5745	.6037	.5361	.5938
Organic C.		1.0000	.2281	.4573	-.7240	-.6940	.0353	.3350	-.3531	.5491	.7301	.6494	-.5554	-.4253	-.6618
Ferric Iron			1.0000	.2234	-.1754	-.4870	.3213	.2595	-.0518	.1577	.3803	.1563	-.2606	-.2422	-.5610
Pyrite				1.0000	-.7741	-.5679	-.2203	-.1151	.0158	.1793	.4145	.5721	-.4054	-.2053	-.4047
Tot. Silicate					1.0000	.5750	.1408	.0544	.2229	-.3967	-.5649	-.5340	.4294	.3391	.4458
Quartz						1.0000	-.0793	-.3363	.0236	-.3514	-.6046	-.5506	.6017	.4650	.7350
Kaolinite							1.0000	.1586	-.0714	.0568	.0304	-.1701	.1660	.1395	-.1380
Illite								1.0000	-.7427	.1742	.2165	.1554	-.1993	-.1525	-.4118
Amorphous									1.0000	-.1959	-.1712	-.1054	.0382	.0302	.1910
Aromatic										1.0000	.6163	.1442	-.2621	-.2033	-.3777
Aliphatic											1.0000	.3629	-.5457	-.4330	-.6489
Log Uranium												1.0000	-.5327	-.3943	-.4348
Molybdenum													1.0000	.8933	.3994
Manganese														1.0000	.2913
Quartz, Grain Size															1.0000

$P_{.05} = .1946$

$P_{.01} = .2540$

$N = 99$

Table III

Simple Correlation Coefficients,

Ohio Shale

	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicate	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size
CO_2	1.0000	.2483	-.3225	-.1485	-.3440	.2154	-.0538	-.3131	.1326	-.0219	.4176	.0853	.4480	.2499	.2382
Organic C.		1.0000	-.5940	.3039	-.5771	.1200	-.4098	-.4010	.2694	.0004	.8259	.7405	.2093	.3916	.4187
Ferric Iron			1.0000	-.2499	.2978	.0621	.4022	.3968	-.4466	.0290	-.6696	-.4954	-.1197	-.2509	-.0588
Pyrite				1.0000	-.6246	-.3843	-.3905	.2148	-.1870	-.2050	.2961	.3587	-.1099	.0141	-.0586
Tot. Silicate					1.0000	.1621	.1883	.0974	.1150	.2743	-.5368	-.4163	-.0345	-.1416	-.2659
Quartz						1.0000	-.1148	-.5110	.1895	.0083	.1046	.0433	.2378	.2743	.4003
Kaolinite							1.0000	.2622	-.3056	.1818	-.4697	-.5743	-.1545	-.2881	-.3514
Illite								1.0000	-.8821	-.0820	-.4396	-.3413	-.2395	-.3414	-.2749
Amorphous									1.0000	.1518	.3481	.3236	.1770	.2776	.0990
Aromatic										1.0000	-.1383	-.0177	.2426	.0737	-.2823
Aliphatic											1.0000	.5886	.3166	.5185	.3932
Log Uranium												1.0000	.2104	.3181	.3826
Molybdenum													1.0000	.4251	.3747
Manganese														1.0000	.3183
Quartz, Grain Size															1.0000

$P_{.05} = .2875$

$P_{.01} = .3721$

$N = 46$

Table IV

Simple Correlation Coefficients,

St. Hippolyte Shale

	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicate	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size
CO_2	1.0000	.1824	-.4288	.1973	-.5497	-.2454	-.1391	-.3273	-.1919	.2429	.2621	.2673	.7530	-.7783	-.2193
Organic C.		1.0000	-.1749	.5808	-.5484	-.4561	.1267	-.3489	-.1513	.4571	.4835	.3436	.2450	.2209	-.1817
Ferric Iron			1.0000	-.3811	-.1768	.0499	-.1074	-.0473	-.2224	-.1361	-.0829	-.0617	-.2007	-.2557	.2785
Pyrite				1.0000	-.2040	-.3332	.3388	-.1937	-.0583	.4877	.6391	-.0144	.1214	.1503	-.2946
Tot. Silicate					1.0000	.6097	.0462	.5701	.3637	-.3118	-.3487	-.5047	-.6103	-.5805	.2837
Quartz						1.0000	-.2311	.0467	.0682	-.2421	-.2510	-.2709	-.2789	-.2863	.5034
Kaolinite							1.0000	-.1791	-.3553	.3128	.3096	-.1246	-.0985	-.1190	-.0993
Illite								1.0000	-.0589	-.3316	-.3233	-.3931	-.4529	-.3800	.0391
Amorphous									1.0000	-.1752	-.2406	.0082	-.1443	-.1524	-.0467
Aromatic										1.0000	.7586	-.0350	.1453	.1451	-.1202
Aliphatic											1.0000	-.2042	.1294	.1114	.1440
Log Uranium												1.0000	.4483	.4914	-.0390
Molybdenum													1.0000	.8973	-.1865
Manganese														1.0000	-.1811
Quartz, Grain Size															1.0000

$P_{.05} = .2845$

$P_{.01} = .3684$

$N = 47$

Table V

Simple Correlation Coefficients,

Alum Shale

	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicate	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size
CO_2	1.0000	-.1994	.0106	-.2006	-.0393	.1576	-.0180	-.0179	-.0721	-.2129	-.1453	.0005	-.0196	.0440	.4883
Organic C.		1.0000	-.3803	-.4352	-.2977	-.0821	-.0225	.0326	-.0716	.2027	.1148	.3160	.0279	-.0045	-.3659
Ferric Iron			1.0000	.4300	-.2965	-.1162	-.1055	-.0396	.0258	.2217	.0487	.0140	-.0976	-.2435	.1168
Pyrite				1.0000	-.3778	-.2413	.0021	.0814	-.0641	.0360	-.1639	-.1730	-.1309	-.1622	-.2191
Tot. Silicate					1.0000	.3367	-.1314	-.0400	.1933	-.1884	.0567	.2666	.1786	.1474	.1309
Quartz						1.0000	-.3146	-.0252	-.3683	-.2485	.0701	-.0917	.0374	-.2034	.0897
Kaolinite							1.0000	.1047	-.0752	.2928	.0343	-.0583	.0274	.1803	.2975
Illite								1.0000	-.8613	.0623	.3587	-.3669	-.1043	.0810	-.0736
Amorphous									1.0000	-.0151	-.3279	.2811	.1233	.0678	.0237
Aromatic										1.0000	.2972	.2143	-.1365	-.0336	-.0521
Aliphatic											1.0000	-.2157	-.0439	.0514	.0349
Log Uranium												1.0000	-.0270	.0184	.0214
Molybdenum													1.0000	.5871	-.0729
Manganese														1.0000	-.0375
Quartz, Grain Size															1.0000

$P_{.05} = .2228$

$P_{.01} = .3427$

$N = 55$

Table VI

Simple Correlation Coefficients, Four Shales Combined

	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicate	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size
CO_2	1.0000	−.1202	−.0654	−.2707	−.3461	−.0814	.1357	−.2662	−.0544	−.0444	−.1534	.1671	.7289	.7263	.0802
Organic C.		1.0000	−.2286	.5606	−.5786	−.3269	−.2016	−.4710	−.3302	.3632	.3410	.6448	−.1324	−.0629	−.2504
Ferric Iron			1.0000	−.4950	−.3525	−.3687	.4177	−.0727	−.1610	−.1793	−.3053	.1296	.2377	.1671	.2413
Pyrite				1.0000	−.0694	.1012	−.5286	−.1735	.2825	.2524	.4314	.1412	−.4620	−.3809	−.2534
Tot. Silicate					1.0000	.7252	−.2840	.6063	−.1658	−.0938	.0853	−.7820	−.4223	−.4409	.1518
Quartz						1.0000	−.4949	.1974	−.1323	.0355	.2270	−.5127	−.2524	−.2863	.3466
Kaolinite							1.0000	−.0612	−.2297	−.1103	−.3519	.0824	.3415	.2860	.0018
Illite								1.0000	−.7395	−.0137	.0949	−.6595	−.2643	−.2540	−.0897
Amorphous									1.0000	−.0701	−.0828	.3833	−.0707	−.0502	−.0381
Aromatic										1.0000	.6613	.0566	−.1167	−.0674	−.1021
Aliphatic											1.0000	−.0608	−.3075	−.2154	−.0860
Log Uranium												1.0000	.3118	.3659	−.0275
Molybdenum													1.0000	.9043	.0803
Manganese														1.0000	.0468
Quartz, Grain Size															1.0000

$P_{.05} = .1270$

$P_{.01} = .1665$

N = 247

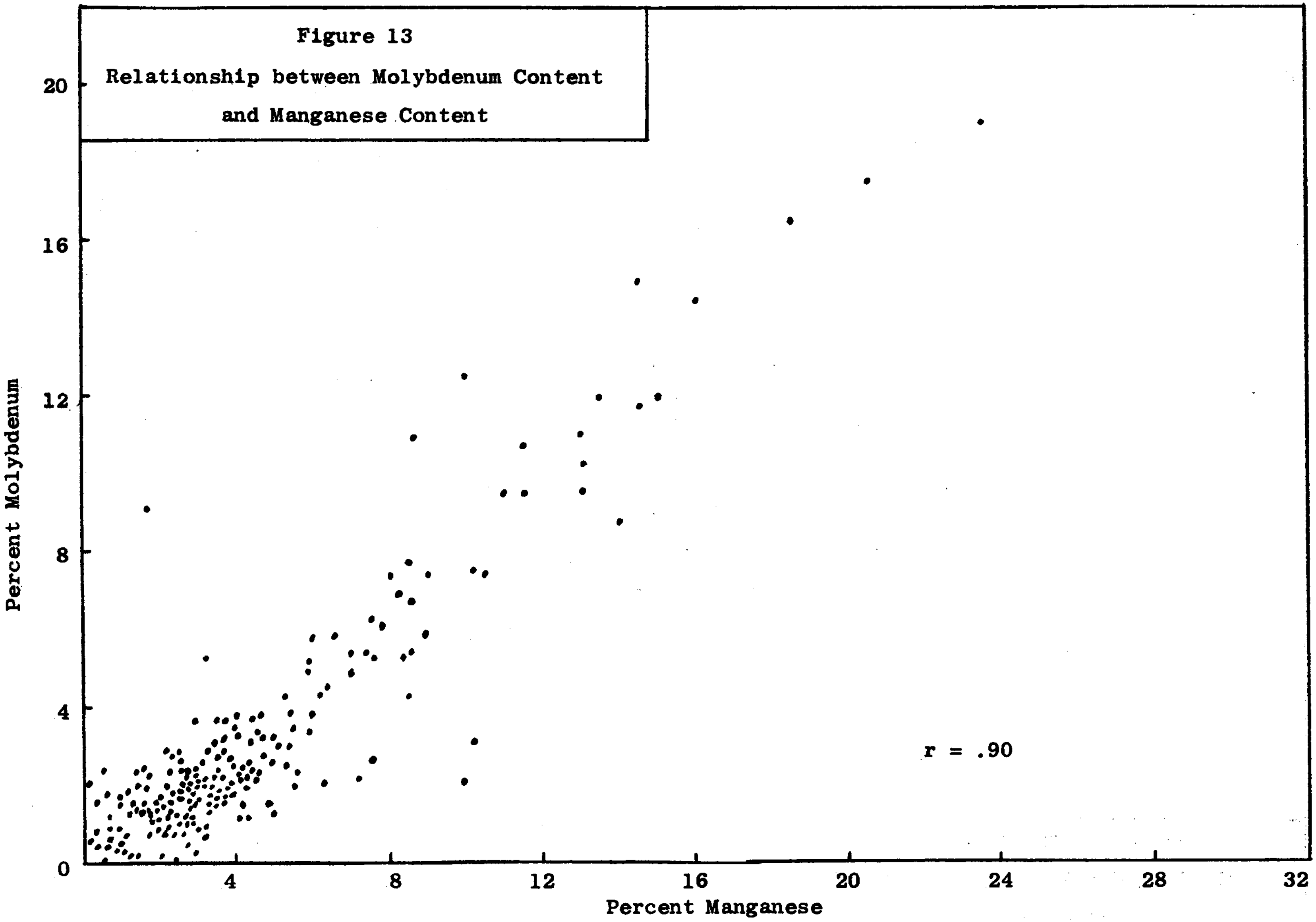


Figure 13

Relationship between Molybdenum Content and Manganese Content

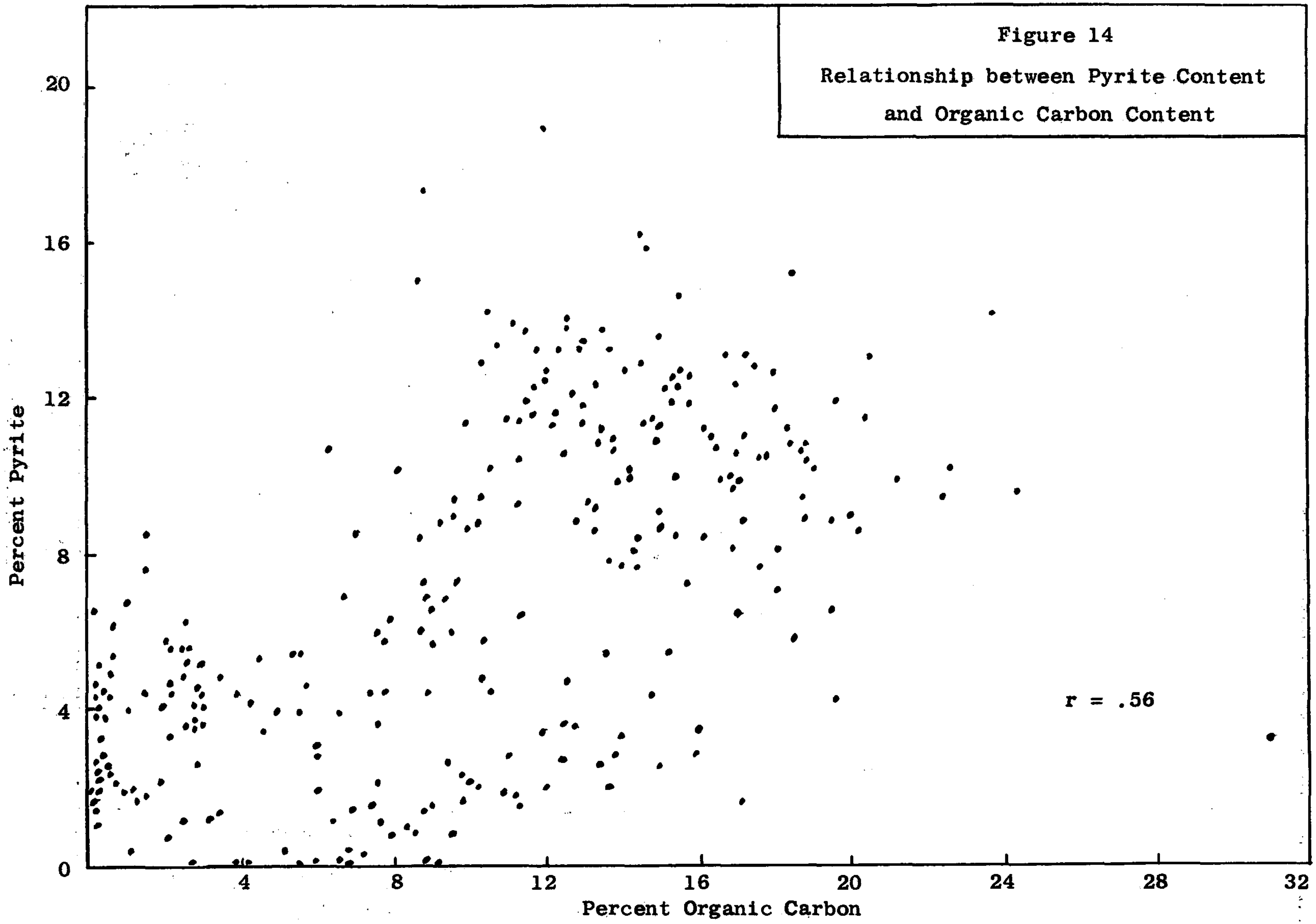


Figure 14

Relationship between Pyrite Content and Organic Carbon Content

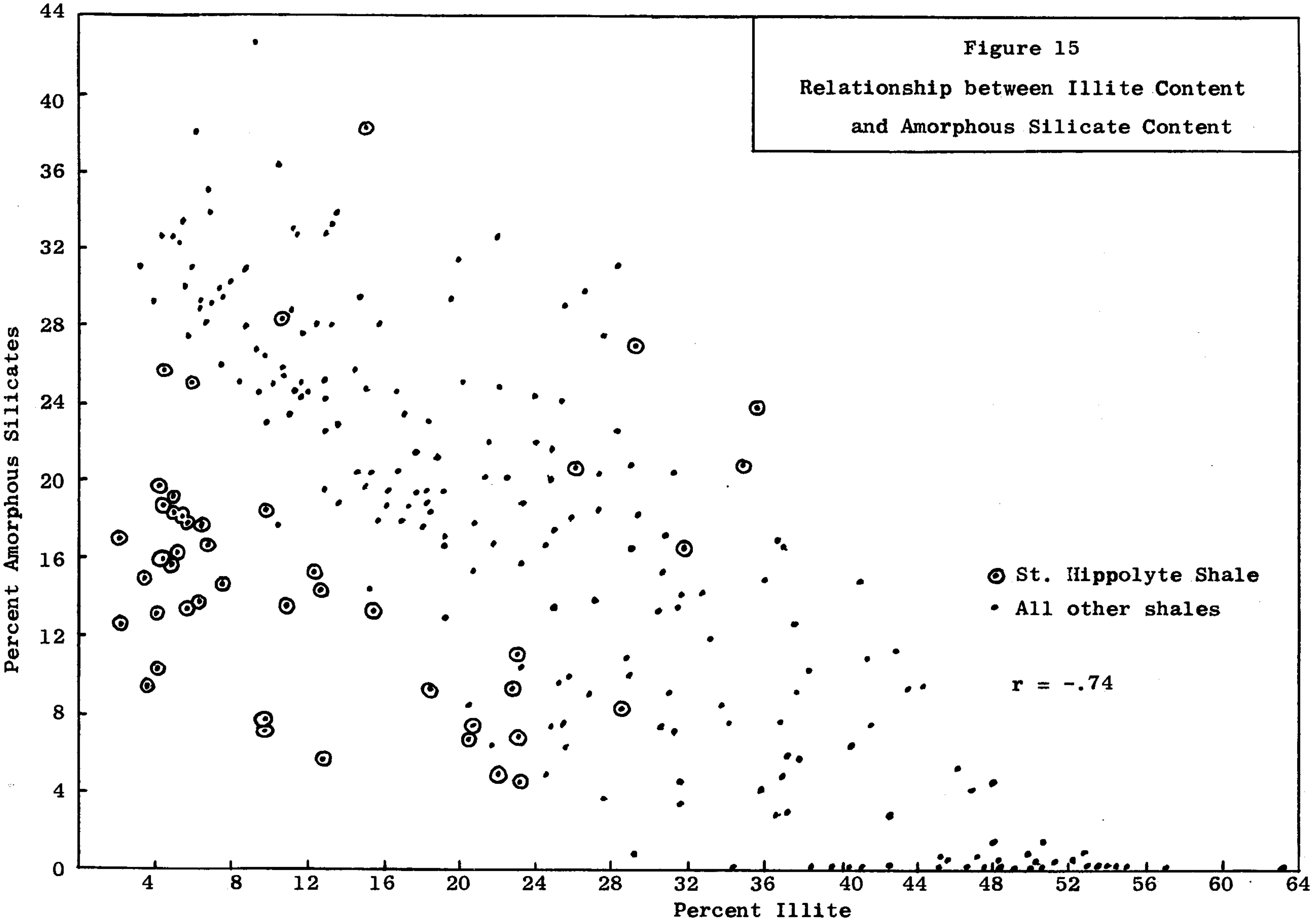


Figure 15

Relationship between Illite Content and Amorphous Silicate Content from the other three considered. A similar behavior of the St. Hippolyte shale can be found in the percent quartz - quartz grain size relationship (figure 16) and in the percent organic carbon - log uranium relationship (figure 17).

The relationship of aliphatic material to organic carbon is apparently specific to each shale. The Ohio and Chattanooga shales show similar aliphatic - organic carbon relationships and the St. Hippolyte and Alum shale also appear to be quite similar (figure 18).

Many of the relationships vary between the shales and are, therefore, discussed separately for each shale in the section dealing with the interpretation of results.

Limitations of the Analysis

The usefulness of the correlation analysis is somewhat restricted by the limitations effected by the nature of the data.

In order to conduct a correlation analysis, the data must vary over an adequate range. The poorer the actual correlation of the variables, the larger the range must be. In the case of the Alum shale, the composition of samples analyzed was found to be quite uniform; that is, the carbonate, organic carbon, pyrite, uranium, molybdenum, manganese, and quartz grain size varied over only a narrow range. The Alum shale samples analyzed, therefore, were not suitably chosen for a correlation analysis and the correlation coefficients determined for the above mentioned variables are highly influenced by the nature of the sampling pattern.

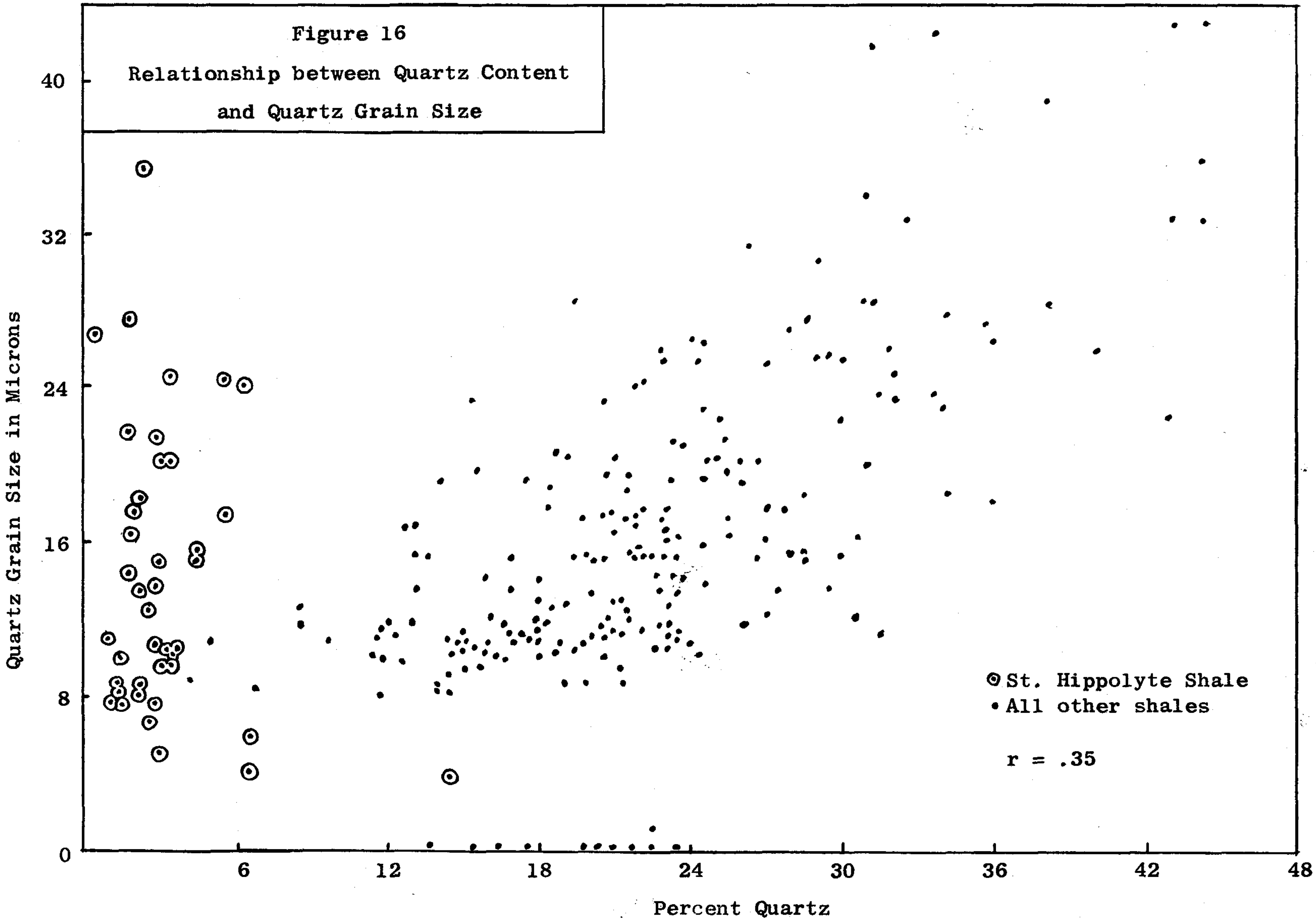


Figure 16
Relationship between Quartz Content and Quartz Grain Size

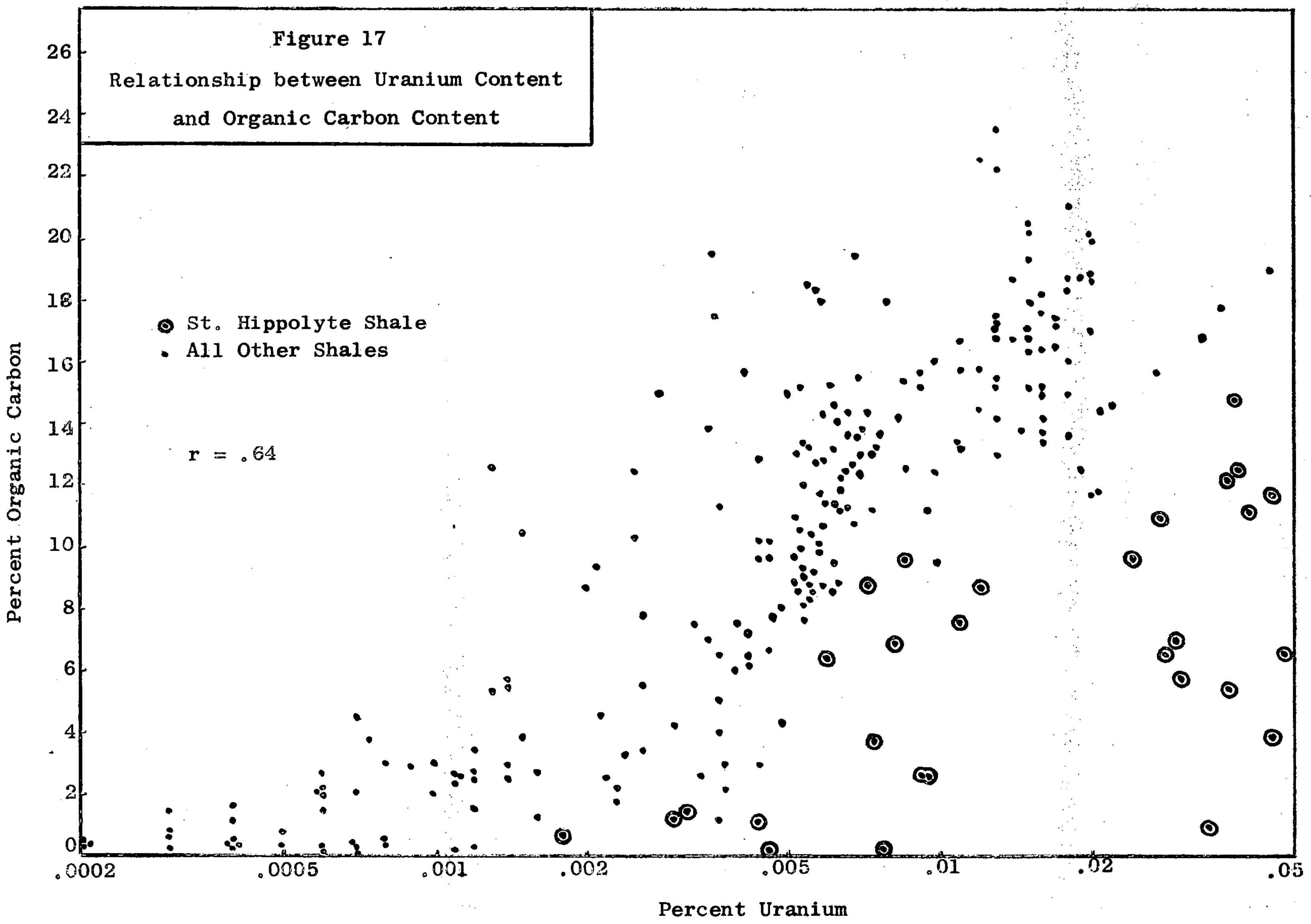
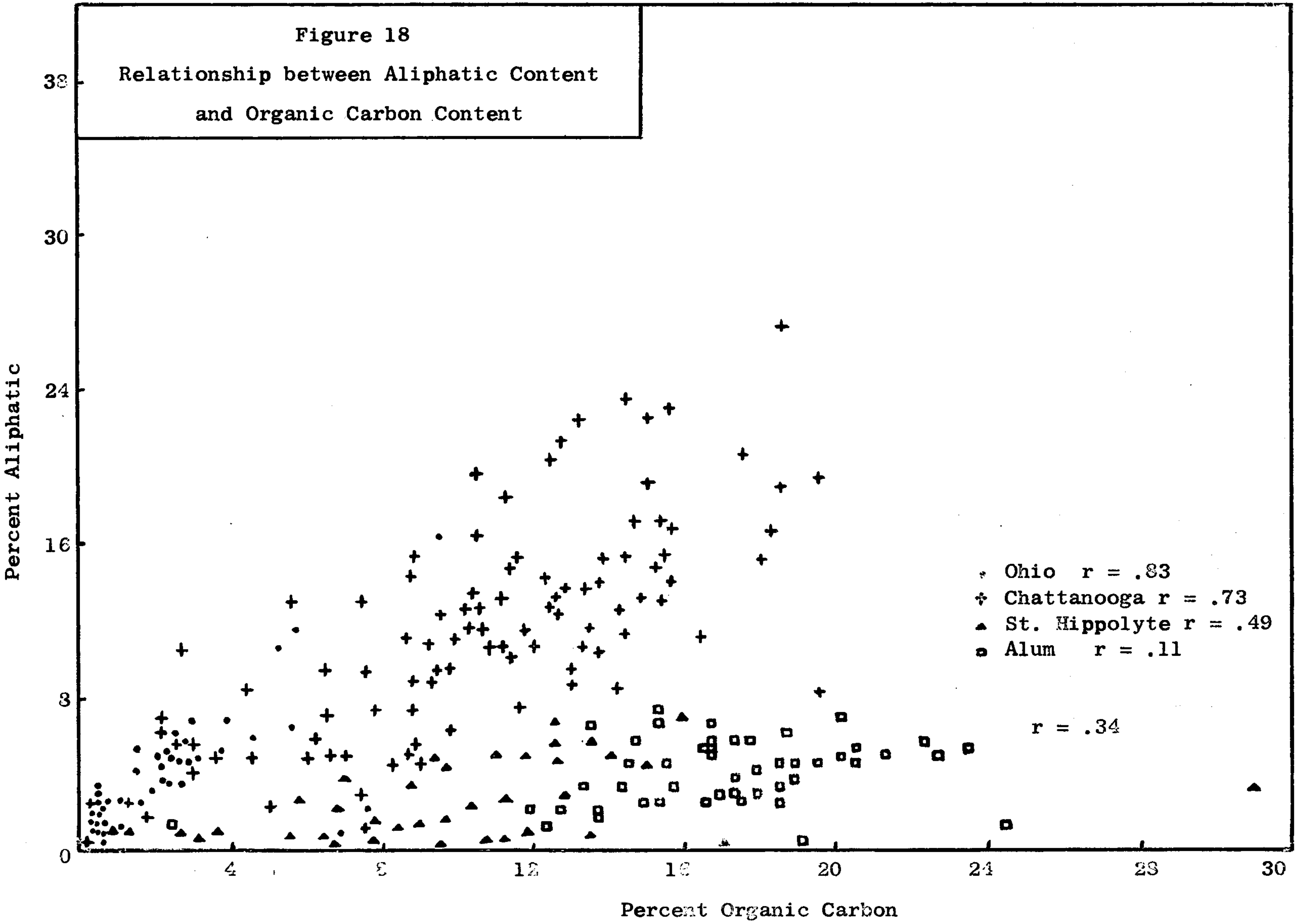


Figure 17

Relationship between Uranium Content and Organic Carbon Content

Figure 18

Relationship between Aliphatic Content and Organic Carbon Content



Another limitation to be considered is quite similar in its effect to the one already mentioned. In order to obtain useable data for correlation analysis, the precision of the techniques used to obtain the data must be sufficiently great enough to detect actual low correlations. In general, the precision of the techniques used in this study was adequate. For several variables, however, where only small quantities of a component were present, the variation in results, due to a lack of extremely high precision, nearly equaled or exceded the natural compositional variation. This effect is particularly noticeable in the analyses of kaolinite and of aromatic material. The quantity of the latter in all shales but the Chattanooga was close to or below the lower limit of detection of the technique employed (0.2%). The amount of aromatic material determined was, therefore, either greater than 0.2% or 0%. This resulted in a large technique error in comparison to a small variation in the amount of aromatics.

The amount of kaolinite present in the Chattanooga and Alum shale was similarly found to be quite small and within the experimental error for the technique used to determine this quantity. The mean value for kaolinite in the Chattanooga shale was found to be 3.2% and for the Alum shale, 3.9%. The two standard deviation limit (the limit that includes 95% of the determined values) was found to be less than 2% for both of these shales. Since the precision in determination is ± 2% ($2S_y$) for kaolinite, the complete range of kaolinite variation in these two shales lies within the error of determination.

A third limitation in the correlation analysis is the inability of the data to meet all the theoretical requirements of the correlation statistics. As required by the statistics, each variable was determined by an independent measurement but an inspection of the data reveals that the distribution of the data may not meet the requirements of being homogeneous and bivariate normal. The lack of homogeneity and normality limits the predictive value of the statistic and lessens the effectiveness of the significance tests. For the purposes of this investigation, it is assumed that data fulfills these assumptions closely enough to allow for limited prediction and approximate testing.

MULTIVARIATE RELATIONSHIPS

General

The multivariate relationships of the variables were determined by calculating the factor loadings of a principal axes (factor) analysis. The factor loadings obtained for each of the shales are given in tables VII through X. The relative importance or percent contribution of each factor is also given in these tables.

The factoring process reduced the dimensions of the matrix from 15 to 6 (5 for the St. Hippolyte shale). These factors almost completely account for the variation of the 15 variables since the correlation coefficients in the residual matrix are negligible. The residual correlation coefficients for the Chattanooga shale are given as an example in table XI.

The variation in the factor loadings and the importance of each factor is discussed in the section dealing with the interpretation of results.

Table VII

Factor Loadings for Chattanooga Shale

FACTOR	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicates	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size	% Contribution
I	-.68	.85	.46	.61	-.69	-.84	.00	.38	-.25	.50	.78	.67	-.76	-.64	-.77	54.5%
II	-.20	.05	.24	-.49	.36	.00	.39	.76	-.60	.12	.03	-.22	.22	.20	.23	15.8%
III	.35	.22	-.11	.29	-.45	.02	.00	-.07	-.28	.27	.15	-.01	47	.57	.09	10.9%
IV	-.07	-.11	.48	.03	.12	-.22	.37	-.25	.52	.03	.12	-.16	.20	.22	-.30	9.0%
V	.11	.08	-.10	-.28	.01	.14	.04	-.17	.07	.51	.34	-.33	-.12	-.19	.10	6.4%
VI	.23	-.17	.27	.15	-.17	.00	.06	.02	-.18	-.12	-.01	-.26	-.08	-.20	.04	3.4%

Table VIII

Factor Loadings for Ohio Shale

FACTOR	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicates	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size	% Contribution
I	.41	.84	-.68	.25	-.50	.24	-.60	-.65	.55	-.07	.88	.74	.39	.54	.48	49.0%
II	-.17	.22	-.12	.75	-.55	-.54	-.14	.59	-.54	-.29	.15	.22	-.23	-.19	-.09	22.2%
III	-.36	-.04	-.31	.15	.21	-.30	-.19	-.23	.55	.13	-.09	.12	-.37	-.21	-.42	12.0%
IV	.35	.05	-.25	-.05	-.12	-.29	.35	.04	.00	.33	.15	-.18	.19	.04	-.35	6.9%
V	-.21	.05	.06	.04	.27	-.08	-.16	.28	-.06	.36	-.05	.24	.29	.26	-.02	6.0%
VI	-.16	.33	.16	-.07	-.09	.08	.28	-.12	-.07	.18	-.04	.19	-.13	-.09	-.01	3.9%

Table IX

Factor Loadings for St. Hippolyte Shale

FACTOR	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicates	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size	% Contribution
I	-.72	-.62	.25	-.52	.78	.55	-.14	.55	.23	-.54	-.55	-.43	-.76	-.75	.36	47.7%
II	-.34	.31	-.04	.55	.15	-.13	.48	.05	-.12	.56	.65	-.43	-.51	-.52	-.10	23.5%
III	-.27	.11	.67	-.27	-.38	.00	.06	-.29	-.33	.06	.06	.18	-.06	-.12	.34	11.7%
IV	.26	-.21	-.06	-.04	.18	.57	.00	-.17	-.12	.26	.27	-.24	.17	.16	.43	9.9%
V	-.18	.25	-.13	.13	.07	.18	-.16	-.38	.47	.06	-.04	.29	-.07	-.09	.15	7.2%

Table X

Factor Loadings for Alum Shale

FACTOR	CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicates	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size	% Contribution
I	.04	-.01	-.03	-.12	.11	-.15	-.09	-.90	.92	-.10	-.42	.38	.20	.10	.06	25.8%
II	.28	.00	-.51	-.57	.57	.43	-.12	.08	-.11	-.37	.06	-.18	.40	.38	.20	21.1%
III	-.43	.68	-.36	-.26	-.14	-.26	.12	.10	.02	.29	.17	.25	.24	.34	-.47	18.7%
IV	-.01	-.35	.17	.24	.02	-.38	.41	.15	.10	.09	.03	-.20	.42	.57	.18	13.9%
V	.38	.17	.00	-.36	-.18	-.10	.35	-.01	-.06	.28	.12	.30	-.20	-.02	.55	12.5%
VI	-.34	-.11	.04	-.13	.38	.03	.12	-.08	.21	.26	.37	-.19	-.16	-.15	.08	8.0%

Table XI

Residual Correlation Coefficients for Chattanooga Shale

CO_2	Organic Carbon	Ferric Iron	Pyrite	Total Silicates	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Log Uranium	Molybdenum	Manganese	Quartz Grain Size
-.09	-.01	-.01	-.02	-.06	-.03	-.03	-.01	-.01	-.02	-.01	-.07	.01	.02	.01
	-.10	-.04	-.05	-.07	-.02	.06	-.02	-.02	.00	.02	.05	.00	-.01	-.01
		-.03	.01	.00	.02	.04	-.01	-.01	.00	.02	.01	.00	-.01	-.02
			-.02	-.02	-.02	-.04	.00	-.01	.02	.01	.01	.00	.01	.01
				-.09	.03	-.03	.05	.04	.00	.01	-.02	.00	.02	.00
					-.03	.00	-.09	-.08	-.01	.02	.02	.02	.00	.01
						.03	-.04	-.02	-.01	-.04	.00	.01	-.01	.06
							-.07	-.07	.01	-.01	-.03	.00	.01	-.01
								-.07	.01	.00	-.01	.00	.01	-.01
									.00	.01	-.02	.01	.00	.02
										-.02	-.02	-.01	.01	-.03
											-.05	.01	.01	.02
												-.02	.01	-.02
													-.01	-.01
														-.02

Limitations of the Analysis

Since the principal axes analysis is calculated from the simple correlation coefficients, the limitations on the correlation coefficients are carried through the factor analysis.

A reflection of these effects can be seen from a comparison of the analysis of the Alum shale (table X) to the analyses of the other shales (tables VII to IX). The factor loadings on the first factor are comparatively low for the Alum shale and the percent contribution is also comparatively low (25%, compared to approximately 50% for each of the other shales). The factors that limit the usefulness of the correlation statistics, therefore, curtail the usefulness of the multivariate approach of factor analysis. The interpretation of the results of the correlation analysis for the Alum shale is restricted to those components which vary over an adequate range, but all the factor loadings are somewhat influenced by the invariate nature of several of the constituents and the significance of the loadings are, therefore, questionable.

A principal axes analysis was not computed for the four shales combined. The results of this analysis would be uninterpretable because of the varied relationships between the shales.

DISCUSSION AND INTERPRETATION OF RESULTS

INTRODUCTION

Each of the various statistical methods used to analyze the data provides a different type of information regarding the relationships of the constituents of shales and the controlling environmental factors. The variation in composition between shales is studied using the means of the constituents in each shale. The relationships between groups of constituents and the environmental factors of each shale are discussed through the use of the correlation statistic, and the importance and interrelationships of the geological factors are determined using the principal axes analyses.

VARIATION IN COMPOSITION BETWEEN SHALES

Introduction

From the data obtained as a result of the compositional analysis, it can be shown that the variation in composition between shales reflects the effects of the geological environment specific to each shale. The results agree largely with those to be expected from the particular geologic environment, but exceptions are noted.

Chattanooga Shale

Results of the analysis of the Chattanooga shale show many of the features accepted as characteristic of a highly reducing marine environment. It is rich in organic matter (10.8% organic carbon), pyrite (8.7%), and illite (23.9%) and contains only small amounts of iron oxides (.67%

ferric or free iron), calcite (.82% carbonate CO_2), and kaolinite (3.2%). The relatively large proportion of amorphous silicate material (16.3%), high uranium content (.0053%), and abundant organic carbon are indicative of a sediment accumulating at a low rate under reducing conditions (Mason, 1952).

Since the bituminous character of a shale is determined by the presence of liquid or near liquid saturated hydrocarbons (Boone, 1952), and since the amount of CS_2 extractable aliphatic material can be considered to be a measure of these hydrocarbons, the determined aliphatic material can be considered to be a measure of the bituminous character of a shale. The Chattanooga shale has been shown by other workers to be quite bituminous in nature, and therefore, for purposes of comparison with the other shales under study the measured amount of "11.6%"* or 133.4 ppm of aliphatic hydrocarbon can be considered characteristic for bituminous shales containing similar amounts of organic material.

Ohio Shale

On the basis of this study, the Ohio shale must be considered to be a bituminous marine shale similar to the Chattanooga but deposited at a more rapid rate. It contains a large amount of illite (41.3%), considerable pyrite (4.4%), and only small quantities of kaolinite (7.0%) and carbonate (.53%). Whereas the organic carbon content (2.0%) is considerably lower than that of the Chattanooga shale, the amount of aliphatic hydrocarbon ("3.7% or 42.2 ppm) is quite high in

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* equivalent percent toluene; see page 34 for explanation.

terms of "per unit of organic carbon" and the organic material can be considered to be of a bituminous nature. The relatively small amounts of organic carbon, uranium (.0008%), and amorphous silicate material (8.3%) are indications of a relatively rapid deposition rate. The apparently large quantity of free iron (2.1%) is perhaps due to the absence of an adequate quantity of sulfur to reduce the iron to the sulfide form, indicating a more oxidative environment.

St. Hippolyte Shale

The data obtained on the composition of the St. Hippolyte shale reflect the distinctly different character of this shale from the Ohio and Chattanooga. The nature of the organic material, as determined by the amount of aliphatic material ("2.5%" or 30.0 ppm) compared to the amount of organic carbon (9.2%), is considerably more carbonaceous than that found in the Ohio or Chattanooga shale. The presence of large quantities of organic carbon and siderite (2.3% carbonate CO_2) indicate a reducing environment, but the relative deficiency in pyrite (1.7%) and abundance of iron oxides (5.2% ferric or free iron) indicate a somewhat more oxidative environment. It can be seen from the data (Appendix), that the iron mineral composition is extremely variable in the St. Hippolyte shale and the high free-iron average is largely due to the presence of a few samples that are highly oxidized and contain little or no pyrite, siderite, or organic carbon.

The large proportion of kaolinite (12.4%) and lesser amount of illite (13.6%) indicates that this shale is of continental rather than of marine origin (Murray, 1953; Degens, et al, 1957).

Like the Chattanooga shale, a slow rate of deposition is indicated by the presence of appreciable organic carbon, amorphous silicates (16.4%) and uranium (.1259%)*.

Alum Shale

The Alum shale is similar to the Chattanooga shale in that it contains: considerable quantities of illite (11.6%) as compared to the amount of kaolinite (3.9%); large quantities of organic carbon (19.9%), pyrite (11.1%), amorphous silicates (26.8%), and uranium (.0188%); and little iron oxide (.72% ferric iron) and calcite (.23%) carbonate CO_2). Therefore, the Alum shale also is believed to have formed at a low rate of sedimentation under highly reducing conditions in a marine environment. The nature of the organic material, however, differs appreciably from that of the Chattanooga shale. Relatively little aliphatic material ("4.1%" or 47.4 ppm) is present as compared to the amount of organic carbon (16.7%). As a result, the organic material in the Alum shale although described by other workers as bituminous, is believed to be considerably more carbonaceous than that of the Chattanooga shale and more nearly comparable to that of the St. Hippolyte material.

General Aspects

The composition of the shales investigated appears to be a re-

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* It has been shown by Bates and the writer (1958) that in addition to the epigenetic meta-autunite appreciable quantities of syngenetic uranium are likely to be present.

flection of the following geologic and environmental factors: (1) the redox potential; (2) the type of organic material available, bituminous or carbonaceous; (3) the position of the basin of deposition, marine or continental; and (4) the rate of deposition. These four factors might be considered to vary independently but interactions between two or more of these factors seem likely.

To further evaluate the compositional relationships and their environmental significance, the bivariate and multivariate relationships are discussed and evaluated.

BIVARIATE RELATIONSHIPS

Introduction

The study of the bivariate relationships reveals the interrelationships among several groups of constituents and demonstrates the relationship of these groups to the environment.

As pointed out in a previous chapter, several of these relationships are consistent from shale to shale. Many of them, however, reflect the specific environment of each shale and must be considered separately.

Chattanooga Shale

In the Chattanooga shale several groups of associated variables are apparent. High positive correlations with organic carbon were obtained for aliphatic hydrocarbon (.73), log uranium (.65) and pyrite (.46). High negative correlations were found for total silicates (-.72), quartz (-.69), quartz grain size (-.66), calcite (-.55), molybdenum (-.56), and manganese (-.42). Relatively low correlations were found for iron oxides (.23), illite (.34), and amorphous silicates (-.35).

The high correlation of aliphatic hydrocarbon to organic carbon indicates that the organic material present in this shale is uniformly bituminous in composition. The correlations between organic carbon, pyrite, and log uranium indicate that these three constituents vary together and reflect the reducing conditions. The inverse relationship between organic carbon and total silicates provides little information regarding the environment of deposition, for, since pyrite, carbon, and total silicate constitute the bulk of the shale, any increase in organic carbon and pyrite would result in a decrease in the amount of total silicates.

The inverse relationship between organic carbon and the intercorrelated constituents, carbonate, molybdenum, and manganese is believed to be a reflection of the redox potential.

In the silicate mineral group, the quartz is positively associated with the amount of total silicates (.57), while kaolinite (.14), illite (.05), and amorphous silicates (.22) appear to be nearly or completely independent of association with total silicates (the kaolinite associations must be disregarded because of the invariance in the quantity of kaolinite as described in the preceding chapter). An increase in the quantity of total silicates present in the shale is then primarily due to an increase in the quartz content. As the quantity of quartz increases, its grain size also increases, indicating, perhaps, a more rapid rate of deposition.

As the illite content increases the amount of amorphous material decreases (r = -.74). Since an increase in the amorphous silicate content is due to a decrease in the rate of deposition (Mason, 1952), marine bituminous shales, deposited at a faster rate than the Chattanooga, might be expected to contain more illite and less amorphous material than the Chattanooga shale in their silicate mineral fractions.

Ohio Shale

The correlation coefficients obtained for the Ohio shale show the general similarity between the nature of the Ohio and Chattanooga shales. Several exceptions, however, appear to be noteworthy.

As in the Chattanooga shale: the variables reflecting the reducing conditions, namely organic carbon, pyrite, and uranium, are directly related; the high correlation between organic carbon and aliphatic hydrocarbon (.83) demonstrates that the organic matter is of uniform composition; and the variables reflecting the rate of deposition, namely illite and amorphous silicates, are inversely related (r = -.88).

Unlike the Chattanooga shale, there is no association in the Ohio shale between total silicates and any of the silicate materials. An increase or decrease in any silicate constituent, therefore, does not necessitate a change in the amount of total silicates present. Within the total silicate mineral group, however, the constituents are interrelated. An increase in quartz content is paralleled by a decrease in illite (as in the Chattanooga shale) and, in addition to the inverse relationship between illite and amorphous material, an inverse relationship between kaolinite and amorphous silicates is present.

The difference between the relationship of total silicates to quartz in the two shales appears to be largely a mathematical function and not related to the geochemistry of the silicate minerals. In the Chattanooga shale the quantity of total silicates varies considerably (s = 7.5%) and a parallel increase or decrease in quartz content (although only 32% associated) can be detected. In the Ohio shale, the amount of total silicates is more uniform (s = 3.5%) and a parallel variation in quartz content would be largely undetectable by correlation statistics.

Within the silicate mineral group, the relationships appear to be geochemically controlled and, as previously stated, appear to be related to the rate of deposition of the shale.

Also unlike the Chattanooga shale, the carbonate content is not inversely related to the organic carbon and the intercorrelations of carbonate, molybdenum, and manganese are poorly defined. The difference in the relationship between organic carbon and carbonate is believed to be due to a function of Eh condition and is discussed further in a later section. The low correlations among carbonate, molybdenum, and manganese are attributed to the invariant nature of the molybdenum and manganese in this shale.

St. Hippolyte Shale

In the St. Hippolyte shale, the nature of the organic material appears to be more variable than in either the Ohio or Chattanooga. The correlation coefficient for organic carbon and aliphatic material (.49) is significantly lower than in the other shales.

The intercorrelations among organic carbon, pyrite, and log uranium are consistent with what would be expected in a reducing environment.

The total silicates are found to vary directly with quartz (r = .61), illite (r = .57), and amorphous silicates (r = .36), and among the components of this group only kaolinite is found to be correlated to amorphous silicates (r = -.36). An increase in total silicates, therefore, may be attributed to all the silicate components but kaolinite. Unlike the marine shales, the kaolinite and not the illite is inversely related to the amorphous silicates. The relationship is, however, poor and the indicator of the rate of deposition, therefore, poorly defined. Since only one continental shale was analyzed, it is not known whether this is characteristic of continental shales or is specific to this shale.

The amount of carbonate mineral and organic carbon are unrelated in this shale, as in the Ohio shale, and the variables carbonate, molybdenum, and manganese are strongly interrelated as in the Chattanooga shale.

Alum Shale

The relative amounts of the constituents of the Alum shale have shown that this material is quite similar to the Chattanooga shale except in the nature of the organic material. The latter in the Alum shale was shown to be more carbonaceous than that of the Chattanooga. Relatively little additional information about the nature of this shale can be gained from a study of the bivariate relationships because of the uniformity of its composition. The relationships in the Alum shale are believed to be similar to those found for the Chattanooga and the erratic correlation coefficients are considered a function of the sampling pattern and technique errors.

The only correlation coefficient determined that is not affected is the one between illite and amorphous silicates. These two components vary sufficiently and were found to be inversely correlated (-.83) as expected in a marine shale.

General Aspects

The organic material is uniform in nature in the bituminous shales and somewhat more variable in the more carbonaceous shales.

A well defined negative relationship exists between illite and amorphous silicates in the marine shales and a poorly defined inverse relationship is found between kaolinite and amorphous silicates in the continental shale studied.

Pyrite, organic carbon, and uranium vary together in the shales studied and reflect the reducing environment of organic rich sediments.

The coarser the sediment (as determined by maximum quartz grain size) the more quartz is present.

Molybdenum and manganese co-precipitate in an environment characterized by the presence of carbonate minerals. The relationship between these three constituents has been demonstrated to be consistent for the shales investigated. In an analysis of the combined shales, correlation coefficients of .73 were obtained for both the molybdenum-carbonate and manganese-carbonate relationships and a correlation coefficient of .90 was obtained for molybdenum-manganese.

The co-precipitation of molybdenum and manganese agrees with the findings of Goldschmidt (1954) and is explained by the combination of several factors: 1) The similar ionic potential (charge/radius) of approximately 7 cause Mn^{+4} and Mo^{+4} to co-precipitate as hydrolyzate elements in both oxydate and deep sea sediments; 2) the elements behave as an oxidation-reduction couple keeping both elements in either the insoluble (Mn^{+4}, Mo^{+4}) or soluble (Mn^{+2}, Mo^{+6}) form; and 3) the free energies of both MnO_2 and MoO_2 are approximately equal, and therefore, both compounds would be equally stable once precipitated.

The presence of carbonate is a reflection of the more oxidative environment necessary to precipitate these elements.

The varying relationship of organic carbon and carbonate is believed to be a function of the varying oxidation conditions between shales. In both the Ohio and St. Hippolyte shales there is a considerable amount of free iron present. This indicates that the reducing conditions were not as severe as in the Chattanooga and Alum shales. Here, the organic carbon and carbonate tend to vary inversely, indicating the instability of one component in the presence of the other in the highly reducing environment. In the St. Hippolyte and Ohio shales, the lack of association between organic carbon and carbonate indicates that in the more oxidative environment the two constituents are compatable.

Since both the redox potential of the environment and the rate of deposition can affect the concentration of organic carbon and perhaps, also, the nature of the organic material itself by oxidation, it is probable that the various geologic factors that determine the composition of a shale are also interrelated. A multivariate analysis was used to investigate this possibility and to determine the importance of these geological factors.

MULTIVARIATE RELATIONSHIPS

Introduction

The results of the principal axes analysis show that relatively few factors can explain the variation in the composition of each shale. The mathematically obtained factors relate only to the variation in the data and are not necessarily synonomous with the geologic environmental factors. If the geologic factors acting upon the composition of a shale are mutually independent, a factor obtained from the principal axes solution should be resolvable in terms of a single geological factor.

The results obtained are not clearly defined in terms of the specific meaning of each factor and it is suspected that this is partly because of the geological interdependence of the environmental factors that effect the compositions of shales and partly because of the nature of the mathematical solution.

Chattanooga Shale

In the principal components analysis of the Chattanooga shale data (Table VII), the first factor was found to account for 54.5% of the variation in the composition of the shale. The second factor accounted for 15.8% of the variation and the two succeeding factors approximately 10% each. The four factors can be considered to contain 90% of the information that the original fifteen variables contained. The interpretation of the first factor is based upon the high factor loadings on the constituents indicative of reducing conditions. High positive loadings were found for organic carbon (.85), pyrite (.61), aliphatic hydrocarbon (.78), and uranium (.67). High negative loadings were found for carbonate (-.68), total silicates (-.69), quartz (-.84), molybdenum (-.76), manganese (-.64), and quartz grain size (-.77). All the constituents in this latter group were shown by the bivariate analysis to be negatively correlated to organic carbon either by virtue of their affinity to oxidative conditions or by the mandatory inverse relationship to organic carbon and pyrite. The only high factor loadings found for the second factor were illite (.76) and amorphous silicates (-.60). On the basis of these loadings, the factor has been interpreted as representing the rate of deposition. These two factors explain 70.3% of the variation in the data and, therefore, largely control the composition of the Chattanooga shale.

Molybdenum and manganese have relatively high loadings on the third factor (.47 and .57, respectively), and iron oxides (.48) and amorphous silicates (.52) appear to be partially influenced by the fourth factor, but geological interpretations of these two factors are not apparent to the writer.

Ohio Shale

The first two factors calculated for the Ohio shale data (table VIII), explain 71.3% of the variation in the data, an amount quite similar to that obtained in the analysis of the Chattanooga shale. The first two factors appear to jointly represent reducing conditions and rate of deposition. The first factor, with its positive factor loadings for organic carbon (.84), amorphous silicates (.55), aliphatic material (.88), and uranium (.74), and negative factor loadings for free iron (-.68), total silicates (-.50), kaolinite (-.60), and illite (-.65), contains the characteristic elements for both rate of deposition and reducing conditions. Similarly, the second factor, having high loadings for pyrite (.75), total silicates (-.55), quartz (-.54), illite (.59) and amorphous material (-.54), also appears to be related to reducing conditions and rate of deposition. This result is to be expected since the amount of organic carbon in the shale should be partially controlled by both the rate of deposition of the silicate materials and the reducing conditions.

As in the Chattanooga shale, 90.1% of the variation can be explained by the first four factors, but the third and fourth factors appear to be void of any geological meaning to the writer.

St. Hippolyte Shale

The factor loadings on the first factor obtained for the St. Hippolyte shale are opposite in sign to those obtained for either the Ohio or Chattanooga shales. The negative loadings for carbonate (-.71), organic carbon (-.62), aromatic (-.54) and aliphatic (-.55) hydrocarbons, uranium (-.43), molybdenum (-.76), and manganese (-.75) indicate that this factor represents oxidizing rather than reducing conditions. The writer does not have sufficient experience with factor analysis to determine whether this reversal is a function of the calculation or a function of the different type of material analyzed. By simply reversing the signs of the factor loadings on the first factor a result similar to that of the other shales can be obtained. Unlike the results of the principal axes solutions for the other shales, the second factor obtained for the St. Hippolyte shale is characterized by high loadings on the aromatic (.56) and aliphatic (.65) hydrocarbons. The second factor may here be related to the nature of the organic material as well as being related to the factor of reduction (related to organic carbon, pyrite, uranium, molybdenum, and manganese). As these two factors account for 71.2% of the variation in the data, the rate of deposition factor (as possibly indicated by factor IV) is relatively unimportant in this shale.

Alum Shale

Since the data obtained for the Alum shale was largely invariant, the factors determined for this shale are less effective. However, the first factor, with its negative loading of illite (-.90) and positive loading of amorphous silicates (.92), is reflective of the rate of deposition. Factors two and three appear to be related to reducing conditions but this relationship is not well defined.

General Aspects

The results of the factor analyses indicate that the reducing conditions are the most important single environmental factor in the deposition of black shale. The rate of deposition appears to be highly intercorrelated with the reducing environment in a shale, such as the Ohio, where the rate of deposition was relatively rapid (as shown by the small amount of amorphous silicates).

The relationships between organic carbon, carbonate, molybdenum, and manganese are made more obvious through factor analysis. In the highly reduced Chattanooga shale, the factor loadings (on the factor assigned to reducing conditions) were found to be opposite in sign for organic carbon and the carbonate-molybdenum-manganese group. In the more oxidized Ohio and St. Hippolyte shales, similar signs were found. This indicates that in the highly reduced shales the carbonate mineral and its associated molybdenum and manganese are incompatable. In the more oxidized shales, they are not only compatible but similarly dependent on the reducing environment.

SUMMARY AND CONCLUSIONS

PURPOSE OF THE INVESTIGATION

The primary purpose of this investigation was to study the relationships between and among the mineral, organic, and trace element constituents of black shales, and to consider these relationships in terms of the possible geochemical environments.

In order to accomplish this goal, three secondary objectives had to be attained. These objectives were:

1) To design and employ new techniques for determining the silicate minerals, organic material, trace elements, and grain size.
2) To analyze a large number of samples from several black shales.
3) To evaluate the data obtained by appropriate statistical methods.

SAMPLES USED IN THE INVESTIGATION

A total of 280 samples taken from four black shales were analyzed. The shales chosen for this study were: the Chattanooga (120 samples) and the Alum (60 samples) bituminous marine shales, the Ohio (50 samples) bituminous to carbonaceous marine shale, and the St. Hippolyte (50 samples) carbonaceous continental shale.

METHODS OF INVESTIGATION

Methods of Sample Analysis

The samples were analyzed for organic content, silicate mineral content, trace element content, and quartz grain size by new techniques designed by the writer. In addition, the results of analyses for total iron, free iron, carbonate carbon, total silicates, and uranium were provided to the writer.

Organic Analysis

A new method of organic material analysis by nuclear magnetic resonance spectroscopy was developed. Using this method, the amounts of aromatic and aliphatic hydrocarbon obtainable from a shale by carbon disulfide extraction can be determined with a precision of ± 8% of the determined value.

Silicate Mineral Analysis

A method was devised by which the amount of quartz, kaolinite, and illite could be determined within ± 1, 2, and 3% respectively. The method consisted of roasting the sample at a temperature of 300°C for one hour in a specially designed furnace, cooling slowly, acid leaching with a mixture of dilute hydrochloric and nitric acids, and obtaining x-ray diffractometer tracings. Since the absolute x-ray peak intensity was used, a measure of the amorphous silicate material was obtained by the difference between the sum of the quantities of quartz, kaolinite, and illite and the amount of total silicates.

Trace Element Analysis

A new method of trace element analysis was synthesized from several existing methods, taking advantage of the best features of the spark-solution and mutual standard methods of emission spectroscopy. By this method, the quantities of molybdenum and manganese in the samples were determined with a precision of ± 5% of the determined value.

Grain Size Analysis

A method of measuring the quartz grain size was developed by application of the extreme value theory to thin section analysis. The method was found to give stable estimates of the maximum quartz grain size.

Recalculation of Data

The data obtained from the chemical analyses made available to the writer were recalculated to the shale constituents: organic carbon, carbonate, pyrite, and iron oxides.

Methods of Data Analysis

Statistical methods were used to determine the relationships between and among the measured shale constituents. Mean values were used to determine the relative amounts of the constituents in the shales in order to evaluate the composition in terms of the presumed geological environment.

The simple correlation coefficient statistic was used to determine the relationships between and among the constituents of the shales in order to study the interrelationships among the constituents and to study these relationships in terms of the environmental factors.

Principal axes analysis was used to determine the relative importance and interrelationships of the environmental factors.

RESULTS

Chattanooga Shale

The results of the analysis of the Chattanooga shale show many of the features accepted as characteristic of the highly reducing marine environment. It contains abundant organic matter, pyrite, illite, and uranium and little iron oxides, calcite, and kaolinite. The organic material, as indicated by the ratio of aliphatic hydrocarbon to organic carbon, is taken as bituminous in nature. The abundant amorphous and organic material attest to the slow rate of deposition of this shale.

The bivariate correlation coefficients show the direct relationships among the variables for which the concentration is dependent upon reducing conditions: organic carbon, uranium, and pyrite. An inverse relationship to organic carbon is shown for the variables indicative of oxidation: calcite, molybdenum, and manganese.

A high correlation between organic carbon and aliphatic hydrocarbon indicates that the organic material is uniformly bituminous in nature.

The measure taken as indicative of the rate of deposition, amorphous silicates, is inversely related to the illite content, indicating that as the rate of deposition increases the illite content decreases.

As determined by a principal axes analysis, the reducing environment is the most important geological factor and accounts for 54.5% of the variation in the composition. A second factor, accounting for 15.8% of the variation, has high factor loadings for illite and amorphous silicates and therefore is believed to represent the rate of deposition.

Ohio Shale

The Ohio shale is commonly regarded as a bituminous to carbonaceous shale quite similar to the Chattanooga but deposited at a more rapid rate. The ratio of aliphatic hydrocarbon to organic carbon is quite similar to that found for the Chattanooga shale, and therefore, the organic material in this shale is also considered to be of a bituminous nature. The decrease in the amount of organic carbon and the associated constituents pyrite and uranium, and the smaller quantity of amorphous silicates indicates that this shale was deposited at a more rapid rate than the Chattanooga. The environment, while still considered as one of reduction, is believed to be less intensely reducing, as demonstrated by the abundance of iron oxide.

The relationships between the constituents of the Ohio shale are generally quite similar to those found for the constituents of the Chattanooga.

As in the Chattanooga shale, the variables reflecting the reducing conditions, namely organic carbon, pyrite, and uranium, are directly related; the variable reflecting the rate of deposition is inversely related to illite and kaolinite; and the high correlation between organic carbon and aliphatic hydrocarbon demonstrates that the organic matter is uniformly bituminous in nature.

The variables molybdenum and manganese are inversely related to organic carbon and directly associated with carbonate, but, unlike the situation in the Chattanooga shale, carbonate and organic carbon are unrelated.

Principal axes analysis showed that two factors account for 71.3% of the meaningful variation in the data. These factors appear to jointly represent reducing conditions and the rate of deposition.

St. Hippolyte Shale

The character of the St. Hippolyte shale is distinctly different from that of the Ohio and Chattanooga. The organic material contains only small quantities of saturated hydrocarbons (as determined by the ratio of aliphatic hydrocarbon to organic carbon) and in accordance with the existing geological information is considered to be carbonaceous rather than bituminous in character. The large proportion of kaolinite and lesser amount of illite indicate that this shale is of continental rather than of marine origin.

However, like the Chattanooga, a slow rate of deposition is indicated by the presence of appreciable quantities of amorphous silicates and organic carbon, and the presence of this organic carbon along with large quantities of uranium indicates a reducing environment. The relative deficiency in pyrite and the abundance of siderite and iron oxides indicates a somewhat more oxidative environment.

In the St. Hippolyte shale, the nature of the organic material appears to be somewhat more variable than in either the Ohio or Chattanooga, and also, unlike the situation in these marine shales, the kaolinite is inversely related to the amorphous silicates.

Uranium, organic carbon, and pyrite are directly related and are here also considered to be controlled by the reducing environment. As in the Ohio shale, there is no association between the carbonate mineral and the organic carbon content; and carbonate, molybdenum, and manganese are directly related.

On the basis of the principal axes solution, the redox factor explains the major portion of the meaningful variation in the data. A second mathematical factor is related to the nature of the organic material and to reduction, suggesting that the nature of the organic material may be influenced by the redox factor. These two factors account for 71.2% of the variation in composition.

Alum Shale

The Alum shale contains large quantities of organic carbon, pyrite, amorphous silicates, uranium, and illite, and little iron oxides, calcite, and kaolinite. Therefore, it is believed to have formed at a low rate of deposition in a highly reducing marine environment. It is quite similar in composition to the Chattanooga shale except that the organic material is more carbonaceous in nature.

The composition of the Alum shale was found to be quite uniform. Since an adequate variation in composition is necessary for correlation analysis, the effectiveness of the correlation statistic was diminished.

The only geologically significant pair of constituents that showed a sufficient amount of variation were illite and amorphous silicates. These two components were found to be inversely related as is to be expected in a marine environment.

The uniformity of the environment similarly limited the effectiveness of the multivariate analysis. The first factor, however, appears to be related to the rate of deposition and the second and third factors appear to represent the reducing conditions.

General Aspects

Pyrite, organic carbon, and uranium vary together in the shales studied and depend upon reducing conditions for their concentration.

Molybdenum and manganese co-precipitate in an environment characterized by the presence of carbonate minerals. The presence of carbonate is a reflection of the oxidative environment necessary to precipitate these elements.

In a highly reducing environment, organic carbon and carbonate are incompatible but in a more oxidizing environment the enrichment in organic carbon is paralleled by an enrichment in carbonate.

In the marine shales investigated, the amount of illite relative to the amount of kaolinite is much greater than in the continental shale.

A well defined negative relationship between illite and amorphous silicates in the marine shales, and a poorly defined inverse relationship between kaolinite and amorphous silicates in the continental shale, was found. In both the marine and continental shales, this is considered to be a function of the rate of deposition.

As the amount of quartz in the sediment increases, the maximum quartz grain size also increases, but the increase in grain size is more rapid in the continental shale than in the marine shales.

The redox environment, as indicated by the results of the principal axes analysis, is the most important factor in the deposition of black shales. The rate of deposition, a second factor, appears to be highly interrelated with the redox environment where the rate of deposition was relatively rapid.

The organic material is uniform in character in the bituminous shales and somewhat more variable in the carbonaceous shales. There is an indication that the character of the organic material in the St. Hippolyte shale may be related to a variation in redox conditions.

On the basis of this study, it is concluded that the compositions of the shales investigated are highly dependent on the geological factors of environment. The redox potential; the nature of the basin of deposition, marine or continental; and the rate of deposition apparently control the mineralogical and chemical compositions of the black shales. The nature of the organic material, bituminous or carbonaceous, appears to be related to both the type of material available and to the oxidation of the sediment during deposition.

These geological factors are interrelated and the composition of a shale is the result of the joint action of these factors during deposition.

GEOLOGICAL IMPLICATIONS

Geologists often relate a sediment to its source by the similarity of the mineral composition of the sediment to that of the possible source areas. Since the composition of a black shale is highly dependent on the environment, the composition can bear little or no relation to the nature of the detrital mineral material provided to the basin of deposition, and therefore, cannot be used as to determine the source area.

The results of this study show, however, that black shales can provide a great deal of information about the nature of a basin of deposition, and, therefore, should be more effectively employed by geologists for this purpose.

SUGGESTIONS FOR FURTHER RESEARCH

This study provides a basis for a meaningful classification of black shales. In order to classify a black shale and fully understand its deposition, it is necessary to discuss it in terms of the factors which controlled its deposition. This is best accomplished by a study of the composition of a shale and the relationships between its components.

On the basis of this work, a classification could be devised from the methods given below.

A measure of the nature of the organic material can be obtained from the ratio of aliphatic hydrocarbon to organic carbon.

The marine or continental nature of the basin of deposition can be determined by the ratio of illite to kaolinite.

The rate of deposition can be approximated by determing the quantity of amorphous silicates present.

The state of oxidation or reduction can be obtained by determining the quantities of organic carbon and carbonate carbon and the organic carbon/carbonate ratio.

In order to classify a shale by this method, it would be first necessary to fix class limits for each variable. This could only be accomplished by the analysis of a great number of samples from a variety of shales.

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Chattanooga Shale

Drill Core # YB-11

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
22-5	0.0092%	6.39%	0.52%	62.04%	1.88%	15.90%	0.11%	12.61%	0.74%	0.25%	15.87%
22-6	0.0085	6.45	0.52	62.56	1.82	15.54	0.19	12.74	0.74	0.43	15.49
22-7	0.0092	6.16	0.58	61.32	1.88	15.29	0.12	11.98	0.83	0.27	15.26
22-8	0.0083	5.34	0.60	66.17	1.72	14.30	0.22	10.18	0.86	0.50	14.24
22-11	0.0044	2.66	0.64	85.94	0.73	3.14	0.18	4.34	0.92	0.41	3.09
22-13	0.0030	2.35	0.34	65.06	0.76	6.56	8.20	4.32	0.49	18.65	4.32
22-14	0.0095	4.93	0.62	69.22	1.42	11.44	0.57	9.26	0.89	1.30	11.28
22-15	0.0046	3.65	0.54	70.68	1.32	0.88	2.50	6.68	0.77	5.68	0.20
22-18	0.0059	4.31	0.71	69.06	1.85	14.48	0.21	7.73	1.02	0.48	14.42
22-21	0.0056	7.70	0.62	53.87	2.20	18.56	0.04	15.21	0.89	0.09	18.55
22-26	0.0054	3.61	0.92	76.00	1.28	8.04	0.94	5.78	1.32	2.14	7.78
22-28	0.0070	4.42	0.82	65.42	1.77	14.36	1.60	7.73	1.17	3.64	13.92
22-30	0.0058	4.21	0.89	62.88	2.10	18.20	0.49	7.13	1.27	1.11	18.07

Chattanooga Shale

Drill Core # YB-11

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
22-5	23.3%	2.6%	20.5%	15.64%	0.34%	23.04%	.014%	.050%	11.4μ
22-6	27.0	2.8	9.7	23.06	0.54	16.58	.004	.012	25.5
22-7	25.9	2.8	24.8	7.82	0.34	17.10	.014	.025	12.1
22-8	24.4	2.8	21.8	17.17	0.38	12.66	.010	.033	23.2
22-11	38.2	3.3	45.4	0.00	0.22	5.98	.012	.027	39.0
22-13	42.9	2.3	6.1	13.76	0.44	8.23	ND*	ND	33.3
22-14	29.8	2.9	10.6	25.92	0.29	18.20	.010	.023	15.7
22-15	31.6	2.9	19.2	16.98	ND	ND	.018	.034	24.3
22-18	29.4	3.8	25.7	10.16	0.46	23.86	.013	.042	14.0
22-21	19.6	2.4	25.5	6.37	1.40	27.40	.001	.027	11.9
22-26	23.1	3.2	28.8	20.9	0.21	9.48	.024	.034	19.3
22-28	30.6	2.8	19.1	12.92	ND	ND	.026	.040	12.7
22-30	22.8	3.4	31.6	5.08	0.42	15.58	.019	.035	13.9

* Not Determined

Chattanooga Shale

Drill Core # YB-14

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
23-5	0.0098%	5.81%	0.60%	61.57%	1.89%	16.24%	0.09%	11.19%	0.86%	0.20%	16.22%
23-8	0.0074	6.21	0.70	62.61	1.58	13.06	0.10	11.84	1.00	0.23	13.03
23-9	0.0070	5.95	0.66	64.99	1.58	13.06	0.18	11.36	0.94	0.41	13.01
23-11	0.0075	4.88	0.62	64.47	1.58	13.32	0.14	9.15	0.89	0.32	13.28
23-12	0.0055	4.71	0.70	68.92	1.65	13.36	0.20	8.61	1.00	0.45	13.30
23-13	0.0042	4.25	0.76	77.17	1.06	6.62	0.16	7.50	1.09	0.36	6.58
23-14	0.0038	2.02	0.68	89.49	0.72	2.33	0.16	2.88	0.97	0.36	2.29
23-15	0.0034	2.47	0.72	86.24	0.69	2.72	0.18	3.76	1.03	0.41	2.67
23-16	0.0040	3.56	0.74	77.10	1.15	7.93	1.00	6.06	1.06	2.27	7.66
23-17	0.0024	2.86	0.88	79.01	0.77	4.16	2.64	4.25	1.26	6.00	3.44
23-18	0.0023	2.44	0.87	85.12	0.70	2.68	1.55	3.37	1.24	3.52	2.26
23-19	0.0052	5.00	0.67	67.29	1.62	13.24	0.26	9.30	0.96	0.59	13.17
23-20	0.0046	5.09	0.64	68.76	1.38	10.38	0.19	9.56	0.92	0.43	10.33
23-21	0.0063	4.30	0.74	69.65	1.54	13.00	0.76	7.65	1.06	1.73	12.79
23-22	0.0057	4.77	0.62	68.62	1.52	12.91	0.28	8.91	0.89	0.64	12.83
23-23	0.0044	4.09	0.70	73.84	1.40	9.78	0.16	7.28	1.00	0.36	9.74
23-30	0.0079	4.59	0.78	62.58	2.04	18.29	0.64	8.18	1.12	1.46	18.12

Chattanooga Shale

Drill Core # YB-14

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
23-5	29.4%	2.5%	24.4%	5.27%	0.66%	11.06%	.007%	.011%	25.8μ
23-8	23.1	3.2	27.2	9.11	0.36	8.96	.004	.026	16.6
23-9	28.7	3.2	25.2	7.89	0.34	9.52	.004	.007	18.9
23-11	24.4	3.7	11.6	24.77	0.38	10.66	.011	.029	14.1
23-12	25.7	3.0	36.0	4.22	0.37	13.80	.016	.041	16.7
23-13	ND*	ND	ND	ND	0.29	9.60	.012	.019	23.5
23-14	ND	ND	ND	ND	0.00	6.20	.018	.021	27.6
23-15	32.6	3.0	28.1	22.54	0.21	5.72	.014	.017	23.8
23-16	30.1	3.2	16.5	27.30	0.00	13.03	.012	.028	22.6
23-17	ND	ND	ND	ND	0.24	5.36	.036	.040	21.9
23-18	28.1	2.6	27.3	27.12	0.24	6.54	.022	.026	27.3
23-19	28.7	3.6	15.1	19.89	0.82	22.30	.003	.021	15.2
23-20	23.0	3.2	22.4	20.16	ND	ND	.016	.048	10.9
23-21	24.2	3.0	24.7	17.75	ND	ND	.016	.017	25.6
23-22	24.9	2.3	18.2	23.22	0.58	21.30	.007	.007	19.4
23-23	31.8	2.7	17.6	21.74	0.30	9.52	.009	.020	26.1
23-30	16.9	2.9	23.4	19.38	0.60	16.78	.022	.041	15.6

* Not Determined

Chattanooga Shale

Drill Core # NV-59

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
20-3	0.0036%	4.27%	0.64%	62.70%	2.08%	17.64%	0.10%	7.80%	0.92%	0.23%	17.61%
20-4	0.0028	4.59	0.56	63.34	1.80	15.11	0.10	8.66	0.80	0.23	15.08
20-5	0.0026	3.30	0.72	81.23	0.96	5.50	0.08	5.54	1.03	0.18	5.48
20-6	0.0041	4.10	0.72	66.85	1.90	15.76	0.12	7.26	1.03	0.27	15.73
20-7	0.0037	5.50	0.63	65.98	1.46	11.30	0.10	10.46	0.90	0.23	11.27
20-8	0.0053	3.10	0.52	71.96	1.70	15.26	0.11	5.54	0.74	0.25	15.23
20-9	0.0055	3.32	0.63	65.90	2.15	18.64	0.37	5.78	0.90	0.84	18.54
20-10	0.0068	3.69	0.68	65.36	2.16	19.52	0.08	6.46	0.97	0.18	19.50
20-11	0.0061	4.52	0.56	59.90	1.81	15.44	0.12	8.51	0.80	0.27	15.41
20-13	0.0058	4.66	0.56	72.20	1.39	10.22	0.12	8.81	0.80	0.27	10.19
20-14	0.0062	5.08	0.67	72.61	1.22	9.60	0.18	9.47	0.96	0.41	9.55
20-15	0.0052	5.90	0.66	68.07	1.30	9.90	0.08	11.26	0.94	0.18	9.88
20-16	0.0053	5.43	0.65	69.42	1.44	10.65	0.12	10.27	0.93	0.27	10.62
20-17	0.0055	8.89	0.82	56.33	1.66	9.34	1.62	17.33	1.17	3.68	8.90
20-18	0.0086	7.26	0.68	59.26	1.36	12.69	0.30	14.13	0.97	0.68	12.61
20-19	0.0062	7.03	0.64	63.00	1.61	11.56	0.32	13.72	0.92	0.73	11.47
20-20	0.0054	6.47	0.63	64.73	1.60	12.08	0.23	12.54	0.90	0.52	12.02
20-21	0.0059	6.92	0.74	62.88	1.59	12.93	0.10	13.27	1.06	0.23	12.90
20-22	0.0056	7.36	0.73	58.66	1.42	10.64	0.68	14.24	1.04	1.55	10.45
20-23	0.0068	6.08	0.74	66.26	1.46	11.15	0.72	11.47	1.06	1.64	10.95

Chattanooga Shale

Drill Core # NV-59

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
20-3	20.7%	2.8%	42.4%	0.0%	2.42%	20.48%	.016%	.015%	12.0μ
20-4	23.1	3.0	40.3	0.0	0.50	19.37	.015	.018	18.1
20-5	31.1	4.0	24.0	22.1	0.22	12.68	.016	.017	20.5
20-6	23.3	4.1	41.0	0.0	0.26	14.06	.022	.028	13.2
20-7	20.8	2.8	33.8	8.6	0.26	10.72	.003	.014	16.9
20-8	22.7	4.1	42.4	2.8	0.28	15.01	.019	.025	17.9
20-9	23.0	4.0	42.4	0.0	1.04	19.04	.008	.018	12.2
20-10	20.7	4.7	37.4	2.6	0.40	8.12	.014	.013	11.9
20-11	21.5	4.1	34.4	0.0	0.64	13.40	.007	.021	12.4
20-13	23.1	2.1	32.6	14.4	0.27	12.46	.025	.015	17.1
20-14	27.1	1.8	15.7	28.0	0.37	12.13	.006	.028	18.0
20-15	20.5	1.9	27.4	18.3	0.21	6.31	.008	.033	19.7
20-16	17.4	3.4	24.0	24.6	0.25	11.75	.010	.008	19.3
20-17	18.3	3.4	8.0	26.6	0.21	15.50	.017	.004	13.3
20-18	22.3	3.2	15.8	18.0	0.45	12.25	.022	.002	15.9
20-19	21.2	3.4	24.8	13.6	0.70	15.59	.012	.024	12.7
20-20	23.8	2.2	19.0	19.7	0.37	10.64	.004	.030	14.5
20-21	22.5	3.6	12.0	24.8	0.47	13.96	.012	.020	12.0
20-22	27.9	2.0	20.4	8.4	0.44	13.56	.018	.036	18.0
20-23	13.3	4.2	19.5	29.3	0.26	10.80	.043	.085	17.1

Chattanooga Shale (continued)

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
20-24	0.0060%	5.84%	0.74%	64.67%	1.49%	11.95%	1.28%	10.95%	1.06%	2.91%	11.60%
20-26	0.0052	7.11	0.66	62.24	1.60	11.26	0.38	13.85	0.94	0.86	11.16
20-27	0.0062	7.71	0.69	59.41	1.15	9.29	2.19	15.08	0.99	4.98	8.69
20-28	0.0059	7.02	0.81	63.08	1.30	10.85	0.34	13.34	1.16	0.77	10.76
20-29	0.0044	6.80	0.78	62.71	1.33	10.64	0.91	12.93	1.12	2.07	10.39
20-30	0.0064	6.96	0.82	61.11	1.36	12.18	1.38	13.19	1.17	3.14	11.80

Chattanooga Shale (continued)

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
20-24	21.3%	4.4%	23.2%	15.8%	0.28%	15.52%	.054%	.086%	13.1μ
20-26	23.3	4.3	16.6	18.0	0.35	13.00	.021	.033	15.6
20-27	22.8	3.1	8.4	25.1	0.21	11.54	.017	.029	26.0
20-28	23.6	3.5	11.8	24.2	0.29	12.96	.016	.010	16.7
20-29	23.5	3.1	9.6	26.5	1.26	19.98	.021	.055	11.9
20-30	21.8	3.6	12.8	22.9	0.66	11.56	.025	.017	17.5

Chattanooga Shale

Drill Core # NV-60

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
21-2	0.0036%	2.60%	0.64%	63.72%	1.92%	19.61%	0.14%	4.21%	0.92%	0.32%	19.57%
21-3	0.0035	5.16	0.60	64.14	1.74	13.96	0.09	9.79	0.86	0.20	13.94
21-4	0.0020	4.51	0.60	71.43	1.43	8.77	0.09	8.40	0.86	0.20	8.74
21-5	0.0015	2.73	0.62	75.89	1.46	10.52	0.12	4.53	0.89	0.27	10.49
21-6	0.0025	2.92	0.68	73.28	1.64	12.53	0.02	4.81	0.97	0.04	12.52
21-7	0.0025	3.35	0.62	75.01	1.50	10.48	0.32	5.86	0.89	0.73	10.39
21-8	0.0062	2.64	0.60	70.27	1.72	14.86	0.59	4.38	0.86	1.34	14.70
21-10	0.0069	3.24	0.69	71.71	1.76	13.63	0.10	5.48	0.99	0.23	13.60
21-11	0.0098	4.76	0.57	72.00	1.45	9.62	0.23	9.00	0.82	0.52	9.56
21-12	0.0066	4.55	0.66	67.77	1.74	14.42	0.07	8.36	0.94	0.16	14.40
21-13	0.0065	5.59	0.64	67.39	1.50	12.51	0.12	10.63	0.92	0.27	12.48
21-14	0.0066	3.65	0.66	67.12	1.54	11.38	0.14	6.42	0.94	0.32	11.34
21-15	0.0056	4.78	0.62	78.38	1.26	9.36	0.10	8.94	0.89	0.23	9.33
21-16	0.0053	4.61	0.53	78.70	1.36	10.08	0.18	8.76	0.76	0.41	10.03
21-17	0.0076	5.62	0.58	68.81	1.72	13.92	0.42	10.82	0.83	0.96	13.80
21-18	0.0067	7.11	0.68	68.81	1.52	12.63	0.12	13.81	0.97	0.27	12.60
21-19	0.0062	6.44	0.68	69.50	1.62	13.34	0.22	12.37	0.97	0.50	13.28
21-20	0.0066	6.84	0.70	66.07	1.72	13.72	0.08	13.19	1.00	0.18	13.70
21-21	0.0070	6.88	0.72	66.83	1.59	12.48	0.14	13.23	1.03	0.32	12.44
21-22	0.0070	6.47	0.72	66.12	1.86	15.58	0.12	12.35	1.03	0.27	15.55

Chattanooga Shale

Drill Core # NV-60

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
21-2	24.3%	4.5%	16.0%	18.9%	1.52%	19.73%	.027%	.043%	10.4μ
21-3	15.5	3.5	33.1	12.0	0.42	15.32	.008	.003	19.9
21-4	20.9	2.8	27.3	20.4	0.34	14.20	.015	.032	13.3
21-5	24.7	3.9	13.4	33.9	0.48	16.24	.013	.018	16.3
21-6	23.6	3.6	30.5	15.6	0.96	20.18	.014	.023	11.4
21-7	25.7	3.6	29.0	16.7	0.40	11.98	.012	.028	17.4
21-8	28.3	3.4	20.6	18.0	0.62	17.10	.016	.028	15.7
21-10	22.6	3.0	37.7	8.9	0.50	11.96	.016	.033	14.5
21-11	24.4	3.1	24.6	21.7	0.28	9.56	.006	.003	26.2
21-12	13.6	3.2	46.1	4.9	0.28	11.66	.014	.028	15.3
21-13	16.0	3.0	38.2	10.2	0.59	12.94	.018	.039	14.2
21-14	21.8	3.0	46.4	0.0	0.24	10.53	.004	.010	15.1
21-15	23.6	2.8	31.6	20.4	0.25	10.67	.009	.025	13.8
21-16	28.6	2.5	29.3	18.3	0.24	10.72	.010	.031	15.8
21-17	22.2	2.8	25.7	18.1	0.66	14.03	.018	.025	15.7
21-18	25.5	3.2	28.9	11.2	0.37	13.53	.029	.047	20.0
21-19	19.0	3.9	13.2	33.4	0.50	13.78	.013	.041	20.7
21-20	18.2	3.0	37.1	7.8	0.43	10.12	.027	.076	10.3
21-21	14.6	2.6	25.5	24.1	0.45	12.39	.024	.028	10.4
21-22	21.0	3.4	34.0	7.7	0.74	15.78	.028	.042	9.7

Chattanooga Shale (continued)

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
21-23	0.0072%	6.79%	0.82%	65.40%	1.70%	14.52%	0.16%	12.82%	1.17%	0.36%	14.48%
21-24	0.0064	6.20	0.74	69.06	1.48	11.48	0.36	11.73	1.06	0.82	11.38
21-26	0.0064	6.07	0.66	68.47	1.54	12.51	0.84	11.62	0.94	1.91	12.28
21-27	0.0063	6.60	0.70	65.17	1.70	14.26	0.50	12.67	1.00	1.14	14.12
21-28	0.0022	2.61	0.88	86.85	0.72	2.68	0.12	3.72	1.26	0.27	2.65
21-29	0.0050	5.00	0.75	68.46	1.66	15.03	0.10	9.13	1.07	0.23	15.00

Chattanooga Shale (continued)

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
21-23	23.4%	3.5%	31.3%	7.2%	0.60%	15.90%	.013%	.021%	14.4μ
21-24	23.6	3.2	45.2	0.00	0.40	15.24	.018	.028	15.5
21-26	20.9	3.6	30.4	13.6	0.29	14.10	.024	.057	20.6
21-27	21.3	3.6	12.3	28.0	0.28	8.21	.020	.038	9.1
21-28	26.5	5.9	25.4	29.1	0.24	10.16	.013	.021	31.6
21-29	18.7	3.7	31.7	14.4	1.96	22.74	.018	.036	13.0

Chattanooga Shale

Drill Core # A1-64

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
89.2	0.0042%	2.64%	0.55%	80.01%	7.61%	0.70%	4.49%	0.79%	1.59%	7.42%
90.1	0.0049	5.30	0.53	71.37	8.37	0.80	10.25	0.76	1.82	8.15
90.2	0.0047	2.74	0.62	78.43	8.06	0.79	4.55	0.89	1.80	7.84
91.0	0.0063	3.15	0.48	74.76	9.45	1.76	5.74	0.69	4.00	8.97
91.9	0.0054	3.58	0.48	72.70	9.30	0.80	6.66	0.69	1.82	9.08
92.5	0.0037	2.40	0.47	82.13	5.41	1.18	4.15	0.67	2.68	5.09
93.0	0.0046	3.56	0.26	70.74	7.77	3.74	7.09	0.37	8.50	6.75
94.6	0.0056	3.70	0.31	70.92	9.19	1.20	7.28	0.44	2.73	8.86
95.6	0.0053	3.06	0.22	77.63	8.89	0.72	6.10	0.31	1.64	8.69
98.3	0.0059	3.57	0.32	75.22	9.09	0.80	6.98	0.46	1.82	8.87
99.2	0.0011	1.45	0.67	84.37	1.66	5.19	1.68	0.96	11.80	0.24
101.1	0.0023	1.73	0.65	86.05	2.61	2.50	2.32	0.93	5.68	1.93
102.6	0.0016	1.51	0.63	86.41	1.62	0.78	1.89	0.90	1.77	1.41
102.9	0.0016	1.98	0.74	84.81	3.66	2.82	2.66	1.06	6.41	2.89
103.7	0.0014	2.09	0.34	79.03	4.29	4.59	3.76	0.49	10.44	3.04
103.9	0.0007	4.53	0.19	67.34	3.26	11.62	9.32	0.27	26.42	0.09
106.2	0.0026	3.71	0.75	76.82	8.13	0.78	6.36	1.07	1.77	7.92

Chattanooga Shale

Drill Core # A1-64

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
89.2	36.1%	3.4%	17.0%	23.5%	0.20%	3.12%	.025%	.027%	26.6µ
90.1	30.9	3.7	12.6	24.2	1.00	4.30	.040	.054	28.9
90.2	29.2	3.9	20.1	25.2	0.00	1.26	.059	.066	30.9
91.0	40.3	3.1	27.7	3.7	0.21	4.42	.076	.102	26.0
91.9	28.9	3.7	18.5	21.6	0.21	4.40	.044	.062	25.8
92.5	37.9	3.7	23.2	17.3	0.21	2.22	.047	.064	28.5
93.0	33.5	2.5	11.2	23.5	0.22	5.24	.070	.082	42.8
94.6	32.3	3.2	31.5	13.9	0.43	5.20	.068	.084	25.2
95.6	31.2	2.4	14.6	29.4	0.31	5.00	.033	.050	41.9
98.3	30.9	3.0	13.2	28.1	0.24	4.57	.039	.046	33.6
99.2	53.7	3.4	9.4	17.9	0.00	2.20	.150	.145	26.6
101.1	43.2	4.5	30.8	7.6	0.21	1.94	.096	.115	22.7
102.6	54.4	3.5	21.9	6.6	0.00	2.50	.110	.086	31.7
102.9	30.0	3.5	19.9	31.4	0.21	4.88	.078	.085	25.6
103.7	53.7	3.3	7.3	14.7	0.21	4.00	.058	.060	69.5
103.9	43.4	2.4	3.3	18.2	0.00	0.00	.096	.110	43.0
106.2	27.1	4.5	44.8	0.4	0.24	7.28	.038	.045	12.6

Chattanooga Shale

Drill Core # Al-66

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
80.3	0.0039%	2.01%	0.56%	67.71%	7.16%	4.01%	3.11%	0.80%	9.12%	6.06%
80.8	0.0042	5.54	0.56	67.57	6.33	0.26	10.70	0.80	0.59	6.26
82.7	0.0023	2.88	0.38	67.02	6.33	6.72	5.37	0.54	15.28	4.50
86.0	0.0035	4.33	0.30	77.59	7.36	0.90	8.66	0.43	2.05	7.11
87.6	0.0064	3.46	0.44	81.10	9.14	NS*	6.49	0.63	NS	NS
89.6	0.0058	5.92	0.52	68.66	11.86	0.52	11.60	0.74	1.18	11.72
91.6	0.0058	2.52	0.31	76.48	10.58	0.88	4.75	0.44	2.00	10.34
92.7	0.0054	3.47	0.23	74.44	9.62	0.86	6.96	0.33	1.96	9.38
93.5	0.0054	2.25	0.19	79.17	9.10	0.82	4.42	0.27	1.86	8.88
94.2	0.0037	2.25	0.34	80.72	6.88	1.14	4.10	0.49	2.59	6.57

* No sample

Chattanooga Shale

Drill Core # A1-66

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
80.3	43.9%	2.5%	5.1%	16.2%	0.22%	4.92%	.006%	.010%	36.6μ
80.8	32.5	2.7	12.8	19.6	0.24	5.84	.001	.007	33.1
82.7	44.1	2.6	4.4	15.9	0.21	4.47	.029	.041	43.0
86.0	44.4	3.7	15.1	14.4	0.22	5.16	.033	.047	33.5
87.6	38.1	2.3	16.4	24.3	0.26	5.64	.010	.008	ND*
89.6	33.9	2.2	13.6	18.9	0.24	7.74	.009	.024	27.9
91.6	27.1	2.5	22.0	24.9	ND	ND	.016	.020	16.5
92.7	ND	ND	ND	ND	0.30	8.72	.027	.031	21.1
93.5	35.6	2.5	24.2	16.9	0.32	9.10	.021	.023	27.4
94.2	34.1	2.5	11.4	32.7	0.22	7.08	.034	.037	18.7

* Not Determined

Ohio Shale

Drill Core # 560 Lorain Co., Ohio

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
11-47	0.0007%	3.42%	1.80%	80.31%	1.06%	4.61%	0.20%	3.48%	2.57%	0.45%	4.56%
11-53A	0.0010	4.53	2.33	78.20	1.08	2.26	0.26	4.72	3.33	0.59	2.19
11-58	0.0012	4.95	2.04	73.34	1.10	2.66	0.16	6.25	2.92	0.36	2.62
11-62	0.0014	3.65	1.78	75.48	1.08	5.64	0.40	4.02	2.54	0.91	5.53
11-65	0.0004	4.20	2.16	79.14	0.56	0.78	0.50	4.38	3.09	1.14	0.64
11-68	0.0002	3.92	2.68	79.26	0.52	0.44	0.42	2.66	3.83	0.96	0.32
11-72	0.0033	3.67	1.96	75.58	1.42	7.78	0.55	3.67	2.80	1.25	7.63
11-75	0.0006	4.30	2.14	80.03	0.73	0.42	0.10	4.64	3.06	0.23	0.39
11-79	0.0005	4.93	2.36	77.08	0.84	0.79	0.20	5.52	3.37	0.45	0.74
11-82	0.0004	4.54	2.61	77.96	0.86	1.15	0.10	4.14	3.73	0.23	1.12
11-87	0.0006	4.30	2.20	76.18	0.92	1.51	0.10	4.51	3.15	0.23	1.48
11-91	0.0006	4.38	2.41	79.29	1.10	2.03	0.06	4.23	3.45	0.14	2.01
11-95	0.0002	3.14	1.96	84.86	0.76	0.39	0.16	2.53	2.80	0.36	0.35
11-98	0.0006	4.17	2.41	79.30	0.98	2.80	0.10	3.78	3.45	0.23	2.77
11-102A	0.0006	4.45	2.32	78.45	0.98	2.17	0.06	4.58	3.32	0.14	2.15
11-105.5A	0.0003	4.45	2.10	79.74	0.91	0.61	0.04	5.05	3.00	0.09	0.60
11-112A	0.0012	5.82	1.88	74.38	0.95	1.62	0.08	8.46	2.69	0.18	1.60
11-123A	0.0007	4.45	1.79	82.26	0.99	2.21	0.12	5.71	2.56	0.27	2.18
11-135	0.0004	3.62	2.35	82.39	0.82	0.48	0.59	2.73	3.36	1.34	0.32
11-138	0.0004	5.36	2.16	76.99	0.87	1.12	0.18	6.87	3.09	0.41	1.07

Ohio Shale

Drill Core # 560 Lorain Co., Ohio

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
11-47	20.6%	7.7%	50.4%	1.6%	0.0%	5.90%	.019%	.007%	15.5µ
11-53A	19.9	6.5	41.1	10.7	0.0	4.24	.020	.025	15.9
11-58	20.6	5.4	40.7	6.6	0.0	4.82	.025	.006	23.3
11-62	21.5	5.8	30.6	17.6	0.22	6.32	.024	.029	19.9
11-65	34.0	10.2	31.3	3.6	0.0	0.36	.018	.035	23.3
11-68	31.4	11.6	39.8	0.0	0.21	1.12	.039	.040	11.7
11-72	26.0	7.4	37.2	5.0	0.23	2.12	.024	.030	20.6
11-75	20.8	7.4	51.4	0.4	0.0	0.92	.016	.022	17.7
11-79	19.7	6.6	54.0	0.0	0.0	2.50	.017	.028	17.4
11-82	21.8	9.3	48.8	0.0	0.20	1.06	.026	.049	17.1
11-87	21.9	6.7	48.0	0.0	0.0	4.15	.028	.039	17.6
11-91	23.7	8.6	48.0	0.0	0.02	2.96	.018	.023	21.1
11-95	23.3	10.8	36.0	14.8	0.48	1.50	.021	.015	0.0
11-98	22.6	10.4	45.7	0.6	0.0	4.52	.026	.023	21.7
11-102A	18.6	6.1	37.0	16.8	0.23	4.86	.021	.029	18.0
11-105.5A	21.6	9.1	50.1	0.0	0.0	0.70	ND*	ND	0.0
11-112A	17.6	5.5	51.1	0.2	0.21	2.42	.020	.012	0.0
11-123A	13.9	5.0	63.3	0.1	0.0	3.60	ND	ND	0.0
11-135	22.2	9.8	50.0	0.4	0.0	1.51	.005	.004	0.0
11-138	14.0	6.6	57.2	0.0	0.0	1.51	.027	.026	19.2

* Not Determined

Ohio Shale (continued)

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
11-141	0.0006%	4.68%	1.96%	78.74%	0.94%	2.22%	0.36%	5.84%	2.80%	0.82%	2.12%
11-148	0.0004	3.23	1.96	79.58	0.81	0.36	0.16	2.73	2.80	0.36	0.32
11-150	0.0005	4.03	2.00	80.85	0.71	0.40	0.27	4.36	2.86	0.61	0.33
11-164A	0.0003	5.20	2.30	78.10	0.80	0.77	0.30	6.23	3.29	0.68	0.69
11-167A	0.0001	4.12	2.22	81.42	0.70	0.37	0.14	4.08	3.17	0.32	0.33
11-171	0.0002	3.07	2.14	85.49	0.78	0.40	0.24	2.00	3.06	0.54	0.33
11-177	0.0008	4.01	2.18	78.16	0.73	0.60	0.46	3.93	3.12	1.05	0.47
11-180	0.0004	3.66	2.08	85.08	0.88	0.46	0.23	3.39	2.97	0.52	0.40
11-185	0.0002	4.33	1.89	79.23	0.67	0.40	0.26	5.24	2.70	0.59	0.33
11-204	0.0003	3.30	2.44	82.04	0.52	0.44	0.84	1.85	3.49	1.91	0.21
11-212	0.0011	4.74	2.10	77.24	0.72	2.86	0.49	5.67	3.00	1.11	2.73
11-215	0.0006	3.50	1.62	80.70	0.71	0.36	0.34	4.04	2.32	0.77	0.27
11-224	0.0008	4.47	2.02	80.12	0.86	3.06	0.22	5.26	2.89	0.50	3.00
11-225	0.0009	4.01	1.86	80.16	1.00	3.03	0.33	4.62	2.66	0.75	2.94
11-229	0.0012	4.21	1.92	77.02	0.84	3.59	0.35	4.92	2.74	0.80	3.49
11-238	0.0011	4.41	2.07	77.95	0.82	2.68	0.52	5.03	2.96	1.18	2.54
11-257	0.0011	4.70	2.07	79.09	0.83	2.82	0.50	5.65	2.96	1.14	2.68
11-260	0.0012	4.10	2.14	82.41	0.85	2.96	0.70	4.21	3.06	1.59	2.77
11-273	0.0010	4.10	1.99	76.44	0.86	3.18	0.54	4.53	2.84	1.23	3.03
11-279	0.0014	4.26	1.79	76.35	0.71	2.74	0.57	5.30	2.56	1.30	2.58
11-305	0.0015	3.48	1.40	76.88	0.91	4.08	0.64	4.47	2.00	1.46	3.90

Ohio Shale (continued)

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
11-141	20.2%	6.8%	54.8%	0.0%	0.21%	3.78%	.023%	.037%	0.0μ
11-148	17.2	9.3	54.3	0.0	0.0	2.04	.031	.054	11.9
11-150	14.7	11.6	53.6	1.0	0.22	2.20	.022	.028	0.0
11-164A	16.2	9.3	52.1	0.5	0.0	0.60	.018	.010	0.0
11-167A	25.3	6.7	50.0	0.0	0.0	0.46	.023	.030	22.4
11-171	21.9	10.3	53.0	0.3	0.22	2.06	.029	.024	15.6
11-177	25.3	9.5	37.4	6.0	0.0	1.44	.023	.032	20.8
11-180	18.0	8.1	28.2	30.8	0.21	0.88	.029	.036	0.0
11-185	24.1	5.6	48.0	1.5	0.0	0.88	.015	.016	0.0
11-204	36.0	5.8	14.4	25.8	0.0	1.70	.025	.035	18.4
11-212	25.6	4.1	47.0	0.5	0.0	5.76	.031	.028	21.7
11-215	19.8	4.7	26.5	29.7	0.0	2.88	.015	.027	0.0
11-224	22.1	4.2	42.9	10.9	0.0	4.68	.024	.018	24.3
11-225	23.2	4.7	48.0	4.3	0.0	6.76	.031	.023	21.7
11-229	19.4	3.9	36.7	17.0	0.0	5.48	.026	.054	28.6
11-238	22.3	4.7	46.8	4.2	0.0	5.12	.022	.063	18.0
11-257	21.2	4.2	44.3	9.4	0.21	3.56	.036	.043	18.9
11-260	28.8	4.3	41.6	7.7	0.24	5.72	.032	.102	27.7
11-273	22.5	9.2	24.5	20.2	0.0	5.46	.032	.034	25.5
11-279	22.1	4.3	37.3	12.7	0.0	6.00	.023	.042	15.8
11-305	ND*	ND	ND	ND	0.0	6.82	.021	.028	22.7

* Not Determined

Ohio Shale (continued)

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
11-441	0.0007%	4.46%	2.27%	83.24%	0.60%	0.38%	0.42%	4.70%	3.25%	0.96%	0.26%
11-471	0.0003	2.82	1.94	74.93	0.66	2.75	4.60	1.89	2.77	10.46	1.49
11-512	0.0008	3.20	1.96	85.36	0.58	0.52	0.08	2.66	2.80	0.18	0.50
11-527	0.0014	3.76	1.55	73.18	1.13	6.80	4.02	4.75	2.22	9.14	5.70
11-547	0.0012	3.19	2.07	86.24	0.50	0.34	0.10	2.40	2.96	0.23	0.31
11-550	0.0007	3.06	2.19	87.81	0.52	0.40	0.55	1.87	3.13	1.25	0.25
11-564	0.0013	4.16	1.58	75.45	1.03	6.00	2.39	5.54	2.26	5.43	5.35
11-573	0.0021	4.07	1.27	74.63	1.36	9.56	0.32	6.01	1.82	0.73	9.47

Ohio Shale (continued)

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
11-441	20.8%	8.6%	52.8%	1.1%	0.0%	2.00%	.032%	.044%	0.0μ
11-471	21.8	9.5	37.8	5.9	0.0	5.32	.029	.041	24.2
11-512	24.4	4.7	41.3	15.0	0.0	1.80	.029	.025	26.4
11-527	25.0	4.7	21.4	22.1	0.20	11.54	.050	.059	20.9
11-547	26.3	5.7	21.8	32.5	0.20	0.60	.030	.023	19.0
11-550	30.6	4.7	43.5	9.0	0.20	0.99	.030	.038	16.8
11-564	31.2	4.7	30.7	8.9	0.0	10.68	.034	.041	28.6
11-573	26.6	3.9	11.0	33.0	0.0	16.42	.022	.100	20.5

St. Hippolyte Shale

St. Hippolyte, Haute Rhin, France

Drill Core # A_3

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
16-1	0.0038%	6.27%	5.66%	61.61%	1.14%	3.22%	0.18%	1.31%	7.77%	0.47%	3.17%
16-6	0.0060	7.67	7.11	55.24	1.26	6.50	0.22	1.20	9.77	0.58	6.44
16-7	0.0054	6.54	6.06	53.36	1.31	8.38	0.18	1.03	8.34	0.47	8.33
16-12	0.5612	7.50	7.08	27.82	1.36	11.02	5.42	0.90	0.29	14.27	9.54
16-16	0.0032	13.23	13.55	62.09	0.87	0.97	0.32	0.00	18.80	0.84	0.88
16-19	0.0082	7.89	7.16	52.46	1.42	7.04	0.36	1.57	9.58	0.95	6.94
16-20	0.0134	3.26	2.32	70.32	0.92	1.06	0.22	2.02	2.92	0.58	1.00
16-21	0.0030	6.07	5.10	68.72	1.02	1.26	0.14	2.08	7.04	0.37	1.22
16-22	0.0044	5.18	4.97	64.31	0.86	1.66	1.78	0.45	3.88	4.68	1.17

Drill Core # aob_2

16-31	0.0094	10.12	10.12	70.21	0.84	2.74	0.14	0.00	14.22	0.37	2.70
16-32	0.0452	20.00	22.74	39.15	1.38	4.02	0.23	0.00	32.10	0.60	3.96
16-33	0.0205	22.12	20.52	23.94	1.35	16.33	16.42	3.44	0.00	43.22	11.85
16-34	0.0191	12.54	11.27	43.08	1.45	11.73	8.52	2.73	0.66	22.43	9.40
16-36	0.0120	12.74	12.02	45.76	1.38	11.06	8.16	1.55	2.38	21.48	8.83
16-41	0.0018	1.93	0.86	85.26	0.66	0.86	0.50	2.30	0.32	1.32	0.72
16-42	0.0330	4.05	2.58	47.12	2.22	31.12	0.33	3.16	3.09	0.87	31.03

St. Hippolyte Shale

St. Hippolyte, Haute Rhin, France

Drill Core # A_3

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
16-1	2.2%	3.3%	29.1%	27.0%	0.22%	0.68%	.012%	.007%	8.8μ
16-6	25.9	5.4	6.3	17.7	0.0	0.84	.052	.059	15.0
16-7	2.2	4.5	25.9	20.8	0.0	1.42	.017	.036	13.7
16-12	2.3	6.1	2.1	17.3	0.0	0.38	.118	.145	18.2
16-16	ND*	32.8	ND	ND	0.22	1.06	.038	.036	8.5
16-19	3.4	18.6	5.6	24.9	0.21	2.42	.044	.053	20.2
16-20	15.3	20.8	23.0	11.2	0.0	1.00	.023	.035	23.2
16-21	11.4	30.0	22.1	5.2	0.0	0.88	.017	.030	10.0
16-22	12.7	12.8	10.5	28.3	0.0	1.06	.102	.130	16.9

Drill Core # aob$_2$

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
16-31	36.2	3.8	4.4	25.8	0.0	1.06	.053	.032	100.0
16-32	7.1	4.5	22.9	4.7	0.0	0.88	.036	.055	100.0
16-33	1.4	4.8	4.0	13.2	0.36	5.20	.170	.360	8.2
16-34	3.1	13.0	12.6	14.4	0.52	4.92	.110	.130	5.1
16-36	2.6	15.0	20.6	7.6	0.24	3.66	.096	.130	6.8
16-41	33.9	3.0	31.9	16.5	0.0	0.88	.030	.033	24.3
16-42	6.5	13.3	20.3	7.0	0.30	3.34	.035	.046	24.3

* Not Determined

St. Hippolyte (continued)

Drill Core # a_2b_2

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
16-44	0.0686%	17.85%	19.38%	35.56%	1.60%	6.78%	0.12%	0.00%	27.50%	0.32%	6.75%
16-45	0.0486	13.62	14.40	39.34	1.47	6.97	0.98	0.00	18.81	2.58	6.70
16-46	0.0291	10.02	9.88	47.70	1.38	7.24	0.34	0.30	13.51	0.90	7.15
16-49	0.0281	9.14	8.90	48.43	1.42	7.04	0.98	0.52	10.95	2.58	6.77
Drill Core # B_4											
16-51	0.0072	7.60	6.86	53.92	1.62	9.01	0.12	1.59	9.59	0.32	8.98
16-52	0.0110	6.66	6.10	54.12	1.60	7.78	0.22	1.20	8.32	0.58	7.72
16-53	0.0037	3.64	3.72	62.73	1.10	4.13	0.26	0.00	4.85	0.68	4.06
16-54	0.0054	11.71	10.48	42.66	1.96	13.60	0.61	2.64	13.88	1.60	13.43
16-55	0.0116	7.37	6.04	41.89	2.10	16.02	0.26	2.86	8.16	0.68	15.95
16-58	0.0044	14.39	12.81	35.18	1.80	14.56	5.90	3.39	7.61	15.53	12.95
16-59	0.0412	16.68	15.93	29.04	1.56	13.78	9.18	1.61	6.12	24.17	11.27
16-61	0.0391	6.57	4.90	45.34	1.92	12.78	0.48	3.59	6.14	1.26	12.65
16-62	0.0378	8.71	7.42	42.76	1.84	12.50	0.54	2.77	9.63	1.42	12.35
Drill Core # C_4											
16-100	0.0046	3.78	2.66	62.83	1.46	9.78	0.12	2.40	3.59	0.32	9.75

St. Hippolyte (continued)

Drill Core # a_2b_2

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
16-44	4.7%	6.9%	10.9%	13.6%	0.0%	0.48%	.054%	.070%	15.8μ
16-45	3.7	8.3	8.9	18.4	0.0	0.32	.074	.080	24.6
16-46	6.5	4.2	28.6	8.4	0.21	3.86	.059	.090	4.0
16-49	6.5	15.0	13.5	13.4	0.0	0.58	.075	.090	6.1
Drill Core # B_4									
16-51	2.2	15.0	19.1	17.6	0.22	1.80	.120	.150	35.6
16-52	3.1	15.6	15.2	20.2	0.0	1.78	.053	.076	15.0
16-53	14.4	13.4	14.7	20.2	0.0	1.42	.012	.028	4.0
16-54	2.5	16.7	5.4	18.1	0.36	5.86	.108	.115	12.6
16-55	2.0	21.6	3.3	15.0	1.28	6.92	.038	.037	17.9
16-58	ND*	13.7	ND	ND	0.29	2.54	.145	.160	ND
16-59	1.5	9.1	12.8	5.6	0.0	2.82	.230	.260	7.5
16-61	3.4	27.4	4.1	10.4	0.44	4.64	.053	.084	10.3
16-62	3.7	21.6	9.7	7.8	0.26	5.68	.061	.078	9.9
Drill Core # C_4									
16-100	3.9	26.9	22.6	9.4	0.21	4.54	.028	.043	104.5

* Not Determined

St. Hippolyte (continued)

Drill Core # b_1

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
16-66	0.0086%	1.67%	0.90%	68.92%	1.36%	9.90%	0.42%	1.65%	0.52%	1.10%	9.78%
16-68	0.9986	5.26	4.30	48.90	1.62	14.58	3.50	2.06	0.00	9.21	13.62
16-69	1.2052	5.38	4.48	44.06	1.49	12.12	4.27	1.93	0.00	11.24	10.95
16-72	0.4760	10.70	9.90	23.70	1.70	19.06	7.04	1.72	1.38	18.53	17.14
Drill Core # b_1C_0											
16-76	0.0026	4.52	3.83	69.97	0.97	3.60	0.58	1.48	4.42	1.53	3.44
16-78	0.0062	1.87	1.46	66.68	1.26	8.74	0.75	0.88	0.73	1.97	8.54
16-82	0.0074	5.05	4.19	48.84	1.71	11.33	0.31	1.85	5.43	0.82	11.24
16-83	0.2870	14.65	14.21	42.26	1.20	10.40	8.89	0.94	4.19	23.40	7.97
Drill Core # D_0											
16-120	0.0379	8.76	8.84	38.07	1.46	5.54	0.18	0.00	12.31	0.47	5.49
Drill Core # D_0D_2											
16-131	1.5384	3.53	2.50	58.33	1.56	10.36	0.94	2.21	1.87	2.47	10.10

St. Hippolyte (continued)

Drill Core # b_1

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
16-66	4.7%	5.0%	35.4%	23.8%	0.0%	1.88%	.015%	.015%	15.2µ
16-68	1.8	7.8	11.6	27.7	0.21	0.88	.190	.235	27.6
16-69	1.9	5.4	13.7	23.1	0.21	0.48	.105	.268	21.9
16-72	0.5	8.5	2.2	12.5	0.0	0.34	.165	.185	26.9
Drill Core # b_1C_0									
16-76	5.5	9.2	34.6	20.7	0.0	0.84	.038	.029	24.4
16-78	3.2	10.3	15.0	38.2	0.0	1.48	.015	.015	20.3
16-82	2.5	18.6	18.3	9.4	0.21	0.78	.016	.034	21.5
16-83	5.7	23.4	3.6	9.6	0.32	1.26	.245	.310	17.4
Drill Core # D_0									
16-120	1.7	6.3	23.1	7.0	0.0	0.46	.075	.105	14.5
Drill Core # D_0D_2									
16-131	3.3	9.1	12.9	33.0	0.0	0.36	.035	.059	10.3

St. Hippolyte (continued)

Drill Core # F_2E_4

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
16-139	0.0618%	8.36%	7.39%	45.46%	1.82%	10.27%	0.22%	2.08%	10.17%	0.58%	10.21%
16-140	0.0387	6.74	5.53	39.86	2.08	15.02	0.30	2.60	7.36	0.79	14.94
16-141	0.0455	10.95	9.98	39.11	1.94	12.04	0.18	2.08	13.94	0.47	11.99
16-142	0.0300	6.67	6.66	66.69	1.05	6.10	0.76	0.02	8.14	2.00	5.89
16-143	0.0170	13.06	11.52	34.94	1.82	15.56	5.44	3.31	6.60	14.32	14.08
16-144	0.0124	12.62	10.98	34.68	2.08	16.06	0.26	3.52	15.23	0.68	15.99
16-145	0.0243	13.54	13.54	36.62	1.37	11.70	9.22	0.00	2.63	24.27	9.18
16-146	0.0098	14.17	12.44	31.48	1.55	15.09	9.46	3.72	0.62	24.90	12.51
16-147	0.0272	6.32	4.95	50.30	1.82	11.09	0.17	2.94	6.77	0.45	11.04

St. Hippolyte (continued)

Drill Core # F_2E_4

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
16-139	2.9%	19.9%	6.7%	16.7%	0.0%	2.40%	.025%	.041%	10.9μ
16-140	1.7	19.2	5.6	13.4	0.22	4.30	.049	.070	16.6
16-141	2.7	12.4	5.0	19.0	0.0	1.32	.126	.100	7.7
16-142	40.5	5.7	4.7	15.8	0.22	2.68	.032	.051	100.0
16-143	1.4	9.7	4.1	19.7	0.43	5.52	.092	.017	10.0
16-144	1.3	9.9	5.7	17.8	0.44	7.18	.088	.140	8.9
16-145	3.1	16.2	9.7	7.6	0.53	4.80	.120	.135	9.9
16-146	1.1	7.2	4.4	18.8	0.37	6.64	.175	.205	7.9
16-147	2.3	19.9	12.3	15.3	0.30	5.36	.030	.044	8.0

Swedish Shale

District: Narke (Kvarntorp)   Locality: Norra Mossby

Core: III 7.73 - 25.60

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
19-2	0.0078%	0.81%	0.24%	8.18%	0.42%	10.13%	36.21%	1.22%	0.34%	82.34%	0.25%
19-3	0.0095	11.65	0.70	6.61	0.61	5.26	9.80	23.52	1.00	22.28	2.58
19-4	0.0132	6.94	1.14	52.36	2.10	15.40	0.11	12.46	1.63	0.25	15.37
19-5	0.0110	6.22	1.12	60.11	1.88	13.42	0.21	10.95	1.60	0.48	13.36
19-6	0.0116	6.29	1.08	59.26	1.91	13.50	0.16	11.19	1.54	0.36	13.46
19-7	0.0121	6.07	0.80	59.68	1.88	14.60	0.12	11.32	1.14	0.27	14.57
19-8	0.0134	0.78	0.16	12.58	0.38	11.83	32.16	1.33	0.23	73.13	3.05
19-9	0.0167	5.70	0.74	59.40	1.92	16.58	0.14	10.65	1.06	0.32	16.54
19-10	0.0182	4.37	0.70	56.13	1.80	14.38	2.38	7.88	1.00	5.41	13.73
19-12	0.0172	5.30	0.66	60.41	2.09	16.62	0.13	9.97	0.94	0.30	16.58
19-13	0.0166	5.39	0.70	57.38	1.90	15.41	0.14	10.07	1.00	0.32	15.37
19-14	0.0158	5.21	0.58	59.39	2.12	16.95	0.14	9.94	0.83	0.32	16.91
19-15	0.0130	5.38	0.65	59.38	2.22	16.90	0.14	10.16	0.93	0.32	16.86
19-16	0.0166	5.67	0.64	56.56	2.30	18.44	0.18	10.80	0.92	0.41	18.39
19-17	0.0168	5.51	0.62	58.68	2.08	17.80	0.16	10.50	0.89	0.36	17.76
19-18	0.0184	5.23	0.59	56.69	2.50	21.24	0.18	9.97	0.84	0.41	21.19
19-19	0.0204	4.84	0.66	58.87	2.26	18.82	0.16	8.98	0.94	0.36	18.78
19-20	0.0203	4.60	0.60	57.26	2.23	20.15	0.12	8.59	0.86	0.27	20.12
19-21	0.0168	4.36	0.61	64.42	1.78	14.31	0.10	8.06	0.87	0.23	14.28

Swedish Shale

District: Narke (Kvarntorp) Locality: Norra Mossby

Core: III 7.73 - 25.60

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
19-2	ND*	ND	ND	ND	ND	ND	ND	ND	12.4 μ
19-3	ND	ND	ND	ND	0.0	1.52	.001	.020	9.1
19-4	12.2%	5.0%	15.8%	19.4%	0.24%	6.44%	.016%	.029%	11.5
19-5	19.2	3.7	18.2	19.0	0.28	6.64	.019	.005	13.1
19-6	16.9	4.5	12.6	25.3	0.30	6.35	.014	.019	13.9
19-7	20.5	3.1	10.6	25.5	0.0	5.93	.018	.025	12.2
19-8	ND	ND	ND	ND	ND	ND	ND	ND	12.9
19-9	20.7	2.7	6.7	29.3	0.0	2.20	.022	.016	10.2
19-10	20.2	2.8	5.6	27.5	0.0	1.96	.022	.029	15.2
19-12	20.2	3.0	7.5	29.7	0.0	5.22	.015	.029	13.7
19-13	18.1	3.8	6.3	29.2	0.24	7.18	.011	.022	14.3
19-14	19.2	3.3	5.8	31.1	0.22	5.52	.016	.052	9.0
19-15	16.8	3.4	10.7	28.5	0.0	5.24	.014	.013	12.3
19-16	16.7	3.2	8.7	28.0	0.23	2.88	.011	.023	10.6
19-17	18.1	3.2	5.1	32.3	0.0	1.04	.002	.004	12.4
19-18	15.2	3.5	7.9	30.1	0.34	4.78	.020	.014	11.0
19-19	19.7	3.9	5.3	30.0	0.0	3.64	.024	.028	9.1
19-20	16.3	5.1	9.3	26.6	0.40	6.92	.002	.004	12.4
19-21	24.0	3.2	18.5	18.7	ND	ND	.021	.028	11.0

*Not Determined

Swedish Shale (continued)

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
19-22	0.0176%	4.79%	0.64%	60.76%	1.76%	17.26%	0.14%	8.91%	0.92%	0.32%	17.22%
19-23	0.0184	4.59	0.63	62.26	2.10	16.18	0.11	8.51	0.90	0.25	16.15
19-24	0.0511	5.64	0.63	54.46	2.13	14.96	0.10	10.76	0.90	0.23	14.93
19-25	0.0153	4.72	0.55	58.45	2.34	19.50	0.12	8.96	0.79	0.27	19.47
19-26	0.0177	4.31	0.52	62.13	1.98	16.93	0.11	8.14	0.74	0.25	16.90
19-27	0.0209	4.70	0.50	59.38	2.15	20.16	0.08	9.02	0.72	0.18	20.14
19-28	0.0557	5.20	0.74	53.27	2.40	24.32	0.15	9.58	1.06	0.34	24.28
19-29	0.0364	6.29	0.82	55.13	2.05	18.01	0.14	11.75	1.17	0.32	17.97
19-30	0.0168	5.77	0.77	59.80	1.73	13.78	0.11	10.74	1.10	0.25	13.75
19-31	0.0338	5.11	0.62	58.99	1.97	16.94	0.09	9.64	0.89	0.20	16.92
19-32	0.0210	5.65	0.71	56.96	2.04	17.16	0.10	10.61	1.02	0.23	17.13
19-33	0.0188	4.86	0.48	59.87	2.14	18.50	0.14	9.41	0.69	0.32	18.46
19-34	0.0459	5.50	0.74	57.08	2.15	19.17	0.11	10.22	1.06	0.25	19.14
19-35	0.0222	6.15	0.80	60.28	1.84	14.78	0.10	11.49	1.14	0.23	14.75
19-36	0.0196	5.95	0.75	56.66	2.15	18.38	0.14	11.17	1.07	0.32	18.34
19-37	0.0272	6.40	0.84	56.80	1.92	16.08	1.14	11.94	1.20	2.59	15.77
19-38	0.0200	9.80	0.99	54.44	1.57	12.01	0.09	18.92	1.42	0.20	11.98
19-39	0.0168	7.30	0.89	60.25	1.76	13.53	0.11	13.77	1.27	0.25	13.50
19-40	0.0180	6.27	1.03	61.93	1.97	15.13	0.14	11.26	1.47	0.32	15.09
19-41	0.0198	6.52	0.85	62.67	1.73	12.79	0.42	12.18	1.22	0.96	12.68
19-42	0.0134	5.35	0.62	59.55	1.88	14.68	1.76	10.16	0.89	4.00	14.20

Swedish Shale (continued)

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
19-22	5.1%	4.0%	4.4%	47.3%	0.22%	3.20%	.013%	.024%	11.2μ
19-23	18.0	3.3	27.1	13.9	0.21	5.54	.017	.031	11.2
19-24	2.8	7.8	6.0	37.9	0.26	2.50	.020	.049	13.8
19-25	18.4	4.3	17.2	18.6	0.0	4.38	.017	.032	11.2
19-26	20.1	3.4	5.3	33.3	0.21	4.96	.021	.028	11.5
19-27	20.8	3.7	5.5	29.4	0.22	5.04	.013	.028	11.6
19-28	17.2	2.9	3.9	29.3	0.28	1.38	.017	.027	11.1
19-29	15.4	3.1	11.5	25.1	0.23	4.20	.017	.017	10.9
19-30	19.7	2.7	5.0	32.4	0.0	3.36	.014	.030	11.7
19-31	8.5	3.9	10.4	36.2	0.21	2.46	.027	.059	12.0
19-32	19.6	4.1	7.3	26.0	0.21	1.28	.041	.028	10.9
19-33	22.0	4.1	23.2	10.6	0.21	4.56	.026	.044	11.7
19-34	16.8	3.4	4.2	32.7	0.21	0.52	.019	.022	11.0
19-35	22.5	3.7	9.5	24.6	0.22	5.16	.016	.026	10.7
19-36	18.9	3.5	3.1	31.1	0.0	3.12	.026	.016	10.4
19-37	17.9	3.8	10.1	25.0	0.24	3.62	.006	.014	11.7
19-38	15.0	3.7	6.3	29.4	0.22	2.12	.002	.004	10.8
19-39	15.1	3.7	6.7	34.8	0.0	2.10	.043	.046	11.5
19-40	18.0	4.5	36.7	2.7	0.0	0.0	.021	.063	12.1
19-41	8.7	2.5	9.0	42.5	0.22	2.12	.010	.019	12.8
19-42	19.3	4.5	16.1	19.7	0.0	3.96	.019	.049	15.4

Swedish Shale (continued)

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
19-43	0.0138%	7.44%	0.64%	57.44%	2.03%	15.55%	0.14%	14.61%	0.92%	0.32%	15.51%
19-44	0.0134	5.47	0.56	60.17	2.30	17.63	0.16	10.55	0.80	0.36	17.59
19-46	0.0075	0.83	0.14	11.47	0.54	12.97	33.90	1.48	0.20	77.09	3.72
19-47	0.0037	0.76	0.07	10.14	0.50	10.82	35.24	1.48	0.10	80.14	1.20
19-48	0.0013	6.46	0.57	61.01	1.98	12.10	0.16	12.65	0.82	0.36	12.06
19-49	0.0152	5.86	0.70	61.30	2.25	17.25	0.12	11.08	1.00	0.27	17.22
19-50	0.0130	6.57	0.58	60.55	2.24	17.50	0.12	12.87	0.83	0.27	17.47
19-51	0.0183	5.67	0.82	58.20	2.36	18.85	0.14	10.42	1.17	0.32	18.81
19-52	0.0200	5.76	0.69	54.89	2.34	18.86	0.12	10.89	0.99	0.27	18.83
19-53	0.0157	6.63	0.73	54.14	2.31	18.09	0.12	12.67	1.04	0.27	18.06
19-54	0.0150	6.53	0.82	57.62	2.04	15.26	0.12	12.26	1.17	0.27	15.23
19-55	0.0098	8.16	0.73	52.58	2.10	14.79	0.10	15.96	1.04	0.23	14.76
19-56	0.0113	6.76	0.71	55.66	2.19	16.72	0.09	13.00	1.02	0.20	16.70
19-57	0.0148	6.34	0.56	56.25	2.18	17.00	0.14	12.42	0.80	0.32	16.96
19-58	0.0132	6.14	0.60	55.63	2.43	19.68	0.16	11.90	0.86	0.36	19.64
19-59	0.0212	8.36	0.80	48.98	1.96	14.61	0.18	16.24	1.14	0.41	14.56
19-60	0.0151	6.00	0.64	55.48	2.44	20.42	0.16	11.51	0.92	0.36	20.38
19-61	0.0128	5.38	0.62	54.33	2.62	22.64	0.18	10.22	0.89	0.41	22.59
19-62	0.0131	6.94	0.72	59.70	1.86	13.14	0.14	13.36	1.03	0.32	13.10
19-63	0.0165	7.17	0.84	56.44	1.96	15.10	0.18	13.60	1.20	0.41	15.05
19-66	0.0049	0.64	0.10	10.02	0.66	13.98	35.42	1.16	0.14	80.54	4.31

Swedish Shale (continued)

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
19-43	13.1%	3.6%	6.8%	33.9%	0.0%	4.28%	.028%	.007%	12.1μ
19-44	12.8	6.1	21.2	20.1	0.21	5.84	.024	.043	13.9
19-46	ND*	ND	ND	ND	0.0	0.0	ND	ND	13.7
19-47	ND	ND	ND	ND	0.0	0.0	ND	ND	11.1
19-48	15.4	4.9	22.9	17.8	0.0	1.52	.017	.028	11.3
19-49	17.8	4.8	28.6	10.1	0.54	5.68	.015	.032	10.9
19-50	16.0	5.0	8.7	30.9	0.22	2.64	.018	.031	10.7
19-51	3.7	3.4	6.1	45.0	0.21	4.53	.030	.083	10.7
19-52	14.5	5.7	6.6	28.1	0.24	3.60	.017	.028	11.2
19-53	11.8	5.1	16.7	20.5	0.21	2.66	.008	.017	12.3
19-54	14.2	4.3	14.9	24.7	ND	ND	.024	.006	8.6
19-55	12.0	2.4	6.4	31.8	ND	ND	.009	.019	10.4
19-56	15.7	3.8	4.0	32.2	0.46	6.64	.040	.060	10.9
19-57	15.2	3.7	28.5	8.9	0.0	4.92	.023	.072	9.7
19-58	5.9	3.7	9.0	37.0	ND	ND	.021	.039	8.5
19-59	9.6	2.8	25.8	10.8	0.21	4.36	.003	.013	11.1
19-60	4.2	4.3	5.5	41.5	0.21	4.48	.014	.025	9.3
19-61	14.4	3.5	28.5	7.9	0.0	5.30	.016	.020	9.5
19-62	15.8	3.5	9.9	30.5	0.0	3.54	.020	.042	9.6
19-63	16.6	3.8	7.1	28.9	0.22	2.40	.012	.027	10.2
19-66	ND	ND	ND	ND	0.0	0.0	ND	ND	11.2

* Not Determined

Swedish Shale (continued)

Sample Number	Uranium	Total Iron	Ferric Iron	Total Silicates	Hydrogen	Carbon	CO_2	Pyrite	Iron Oxides	Carbonate	Organic Carbon
19-68	0.0156%	6.08%	0.92%	57.70%	2.16%	16.47%	0.10%	11.08%	1.32%	0.23%	16.44%
19-70	0.0138	5.27	0.60	56.81	2.76	23.62	0.14	10.03	0.86	0.32	23.58
19-73	0.0153	6.77	0.68	54.83	2.52	20.60	0.14	13.08	0.97	0.32	20.56
19-76	0.0132	5.24	0.86	54.20	2.75	22.54	0.57	9.41	1.23	1.30	22.38
19-77	0.0132	7.13	1.02	54.00	2.23	17.28	0.12	13.12	1.46	0.27	17.25
19-78	0.0144	5.46	0.48	60.28	2.35	18.78	0.11	10.70	0.69	0.25	18.75
19-80	0.0055	1.47	0.32	21.62	1.18	15.59	26.94	2.47	0.46	61.26	8.24
19-100	0.0046	0.66	0.08	7.37	0.53	9.31	35.29	1.24	0.11	80.25	0.00

Swedish Shale (continued)

Sample Number	Quartz	Kaolinite	Illite	Amorphous	Aromatic	Aliphatic	Molybdenum	Manganese	Quartz Grain Size
19-68	12.5%	3.8%	10.2%	31.2%	0.26%	5.20%	.017%	.020%	10.0μ
19-70	ND*	ND	ND	ND	0.21	5.32	ND	ND	9.9
19-73	11.8	2.7	17.3	23.0	0.22	5.40	.015	.017	8.3
19-76	11.8	4.1	19.2	19.1	0.21	5.96	.022	.032	11.9
19-77	11.6	4.8	16.3	21.3	0.46	3.80	.012	.018	11.2
19-78	14.3	2.1	20.9	23.0	0.21	6.20	.019	.024	8.7
19-80	ND	ND	ND	ND	0.0	0.0	ND	ND	8.5
19-100	ND	ND	ND	ND	0.0	0.0	ND	ND	12.7

* Not Determined