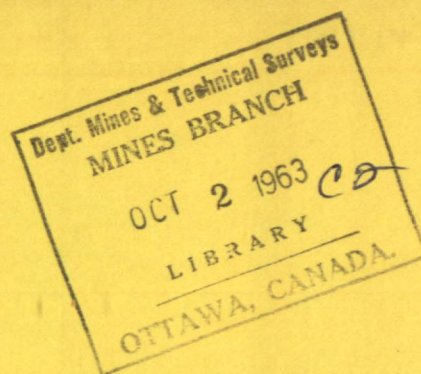




CANADA



**A STUDY OF SEDIMENTED
ORGANIC MATTER AND ITS
NATURAL DERIVATIVES**

**L. H. KING, FRANCES E. GOODSPEED
& D. S. MONTGOMERY**

(WITH APPENDIX BY M. F. MILLSON)

FUELS AND MINING PRACTICE DIVISION

**DEPARTMENT OF MINES AND
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A STUDY OF SEDIMENTED ORGANIC MATTER AND
ITS NATURAL DERIVATIVES

by

Lewis H. King*, Frances E. Goodspeed*, and D. S. Montgomery**
(with appendix by M. F. Millson*)

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ABSTRACT

The need for a classification covering the entire spectrum of organic matter in geological formations has been recognized for some time, but owing to the lack of sufficient data the formulation of such a classification has been held back.

In this report, techniques are described for the preparation of samples of organic matter from geological formations whereby ash contents can be lowered to a level where reliable property measurements can usually be obtained. Property measurements were made on a wide variety of samples which vary in structure from aliphatic to graphitic types. The properties measured include: elemental analysis, volatile matter content, refractive index, density, solubility in carbon disulphide, and infrared spectra.

Structural parameters derived from these properties include aromaticity, reduced molar volume, ring condensation index, an estimate of aromatic cluster size, and quantitative structural group data obtained from the infrared spectra of solid materials mounted in KBr. The correlation of these parameters, as well as of the measured properties, with atom percent carbon delineated structural trends and development tracks for the materials under consideration. These results are compared with the structural and metamorphic trends in coal.

The problem of classification is discussed in terms of genesis and chemical structure. The samples are divided into two major groups on the basis of their origin: sedimented organic matter (syngenetic), and natural derivatives of sedimented organic matter (epigenetic). It appears that further geological qualification is required before the material of syngenetic origin can be properly classified according to its inherent chemical properties, but the study shows that the epigenetic material can be effectively classified in terms of atom percent carbon, volatile matter content, and solubility.

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Direction des mines

Rapport de recherches R 114

ÉTUDE DE MATIÈRES ORGANIQUES CONTENUES
DANS LES DÉPÔTS AINSI QUE DE LEURS DÉRIVÉS NATURELS

Lewis H. King*, Frances E. Goodspeed* et D. S. Montgomery**
(avec annexe préparée par M. F. Millson*)

RÉSUMÉ

On reconnaît depuis quelque temps qu'il faut classer l'ensemble des matières organiques présentes au sein des formations géologiques, mais, faute de données suffisantes, il n'a pas été possible de mettre au point une classification du genre.

Dans le présent rapport, les auteurs décrivent des procédés de préparation d'échantillons de matières organiques en provenance de formations géologiques. Grâce aux procédés en question, les teneurs en cendres peuvent être abaissées à un niveau qui permet ordinairement de procéder à des mesures valables. On a mesuré des propriétés d'une grande variété d'échantillons dont la structure variait du genre aliphatique au genre graphique. Parmi les propriétés mesurées mentionnons l'analyse élémentaire, la teneur en matières volatiles, l'indice de réfraction, la densité, la solubilité dans le bisulfure de carbone, et le spectre infrarouge.

Les paramètres structuraux déterminés à partir des propriétés mesurées comprennent l'aromaticité, le volume moléculaire réduit, l'indice de condensation des anneaux, une estimation des dimensions du groupe aromatique, et des données quantitatives relatives au groupe structural obtenues à partir du spectre infrarouge de matières solides montées sur du KBr. La corrélation entre les paramètres en question, de même qu'entre les propriétés mesurées, et le carbone atomique procentuel a déterminé des tendances structurales et évolutives des matières à l'étude. Les résultats obtenus sont comparés à ceux des tendances structurales et métamorphiques relevés dans le charbon.

Le problème de la classification est étudié en fonction de la genèse et de la structure chimique. Les échantillons ont été divisés en deux groupes principaux compte tenu de leur origine: matières organiques déposées (syngénétiques), et dérivés naturels de matières organiques déposées (épigénétiques). Il faudra sans doute pousser plus avant les études géologiques avant de pouvoir classer convenablement les matières d'origine syngénétique d'après leurs propriétés chimiques inhérentes, mais le présent travail démontre que les matières épigénétiques peuvent être effectivement classées d'après le carbone atomique procentuel, la teneur en matières volatiles, et la solubilité.

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INTRODUCTION

The importance of studies on organic matter in geological formations has long been recognized, especially those investigations pertaining to fossil fuel deposits. The genetic and constitutional aspects of the fossil fuels have received much attention because of the implications concerning the development and conservation of these deposits. Studies on sedimentary organic matter have also been stimulated in recent years by those concerned with atomic energy, because of the association of various radioactive minerals with organic matter in rocks. As our knowledge of the origin of the concentrated accumulations of organic matter has increased, especially in the field of petroleum research, more attention has been devoted to the finely divided organic matter in both recent and ancient sediments, and it is now a widely accepted concept that petroleum is a natural derivative of these syngenetic (primary) sedimentary organic materials.

An intimate knowledge of primary organic matter in sedimentary basins is also necessary to an understanding of many of the so-called "vein hydrocarbons", "hydrocarbon minerals" or "natural bitumens" that are generally of epigenetic (secondary) origin and found in a variety of structural and sedimentary traps. They are sometimes associated with low temperature mineral deposits. Well known members of this group include albertite, gilsonite, wurtzilite, ozokerite, glance pitch, grahamite, impsonite, and anthraxolite. The literature contains many references to isolated deposits of this nature, and a number of classification schemes have been developed to deal with them. In North America, a classification of particular interest was developed by Abraham (1) and later modified by Hunt, Stewart and Dickey (2). These classifications, however, do not encompass the entire range of geological organic matter from either the physicochemical or the genetic point of view; furthermore, they are not universally accepted. Since such a classification as the type envisaged does not exist, communication between geologists is restricted geographically and the best cooperation and understanding between field geologists and geochemists are inhibited.

The need for a classification covering the entire spectrum of organic materials related to geological formations was recognized in 1951 at the Third World Petroleum Congress, but the lack of sufficient critical data in certain areas of the spectrum, as well as an insufficient understanding of the diagenetic and metamorphic processes involved, has prevented the formulation of a quantitative classification. The areas least understood include the finely divided organic matter of the sediments: kerabitumen (see Table 6). Much research has been carried out on the soluble portion of this material, but these fractions are not representative for purposes of classifying the material as a whole, because of the low solubility of kerabitumen.

Only a few attempts have been made to remove the bulk of the organic matter for analysis. Forsman and Hunt (3) have made an extensive contribution in this respect, and Himus (4) has summarized and contributed to the data on the kerogen in oil shales. Breger, Tourtelot and Chandler (5), and Breger and Brown (6), have reported on variations in the hydrogen content of organic isolates from the Pierre and Chattanooga shales respectively.

It is the purpose of this report to present property data on a variety of organic materials from geological formations; to present modified techniques of preparation whereby the ash contents can be reduced to a low level, and to discuss the problem of classification in terms of structural chemistry and geological origin; and, finally, to discuss the development of a scientific classification suitable for the whole spectrum of organic matter in geological formations. The data have been treated, where possible, according to structural methods developed by van Krevelen for coal (7) (8).

DESCRIPTION OF SAMPLES

Table 1 lists the 42 samples used in this investigation, together with their location and descriptive geological information. The samples are designated either according to the nature of the organic matter or according to the rock type or formation in which the organic matter occurs. The samples fall into two major categories according to their origin: syngenetic, where organic material is believed to occur in situ; and epigenetic, for the natural derivatives of primary sedimented organic matter that have migrated. The criteria for making the distinction will be discussed later.

Table 2 shows chemical analyses for the samples in Table 1 that had high inorganic contents and required special preparation for removal of the inorganic components. The analyses show the carbonate, organic carbon, and sulphur contents.

The samples were collected from mines, prospect pits, quarries, and deep road-cuts, hence the extent of surface weathering is not considered to be an important factor.

PREPARATION OF SAMPLES

Many of the samples used in this investigation occur in a relatively pure state and required only hand-picking or hydrochloric acid treatment to lower the ash content to a level where reliable physical and chemical property measurements could be made. The following discussion, therefore, pertains to those samples in which the organic content is low and difficult to isolate. The techniques are basically not new, but certain modifications have been introduced which in some cases represent new applications of existing tech-

TABLE 1
Description of Samples

Sample Designation	Origin of Organic Matter 1/	Occurrence of Organic Matter	Location	Formation	Age
33 Ozokerite	Epigenetic	Vein material, low ash content	Soldier Mine, Wasatch Co., Utah	Wasatch	Eocene
34 Albertite	Epigenetic	Vein material, low ash content	Albert Mines, New Brunswick	Albert	Mississippian
35 Albertite	Epigenetic	Vein material, low ash content	Soldier Summit, Wasatch Co., Utah	Green River	Eocene
36 Wurtzilite	Epigenetic	Vein material, low ash content	Ethyl vein, Duchesne Co., Utah	Green River	Eocene
42 Tahbyite	Epigenetic	Low ash content	Tabby Canyon Mine, Duchesne Co., Utah	--	Eocene
43 Ingramite	Epigenetic	Vein material, low ash content	Soldier Summit, Wasatch Co., Utah	Green River	Eocene
44 Grahamite	Epigenetic	Vein material, low ash content	Ritchie Co., W. Va.	--	--
45 Gilsonite	Epigenetic	Vein material, low ash content	Bonanza vein, Uinta Co., Utah	Green River	Eocene
46 Liverite	Epigenetic	Low ash content	Indian Canyon, Duchesne Co., Utah	Green River	Eocene
49 Grahamite	Epigenetic	Vein material, low ash content	Bathurst Island, Dist. of Franklin, Canada	--	Ordovician
50 Impsonite	Epigenetic	Inclusions in gypsum dome	Axel Heiberg Island, Dist. of Franklin, Canada	--	--
51 Impsonite	Epigenetic	Vein material	St-Joachim de Tourelle, Quebec	--	Ordovician
52 Anthraxolite	Epigenetic	Vein material	Mont Joli, Quebec	--	Ordovician
53 Impsonite	Epigenetic	Vein material	Rimouski, Quebec	--	Ordovician
54 Anthraxolite	Epigenetic	Vugs in chert	Nolalu, near Fort William, Ontario	Gunflint	Precambrian
69 Asphaltic ozokerite	Epigenetic	Veinlets, low ash content	Plymouth, Pictou Co., Nova Scotia	Stellararton	Pennsylvanian
73 Albertite	Epigenetic	Vein material, low ash content	Mathies Coal Co., Finleyville, Washington County, Pa.	Monongahela	Pennsylvanian
77 Albertite	Epigenetic	Vein material, low ash content	General San Martin Mine, Prov. of Mendoza, Argentina	--	--
78 Impsonite	Epigenetic	Vein material, low ash content	La Valenciana Mine, Prov. of Mendoza, Argentina	--	--
79 Impsonite	Epigenetic	Vein material, low ash content	Page, Le Flore Co., Oklahoma	--	--
82 Thucholite	Epigenetic	Inclusions in Uranium ore	Algorn Nordic Mine, Elliot Lake, Ont.	--	Precambrian
83 McMurray Oil Sands	Epigenetic ?	Impregnated sandstone	Mildred Lake, Alta.	McMurray	Lower Cretaceous
85 McMurray Oil Sands	Epigenetic ?	Impregnated sandstone	Abasand Quarry, Ft. McMurray, Alta.	McMurray	Lower Cretaceous
87 Argillite	Syngenetic	Disseminated in calcareous argillite	Brookville Station, near St. John, N. B.	Green Head	Precambrian
88 Carboniferous Fish Scales	Syngenetic	In thin limestone bed	Sussex, New Brunswick	Albert	Mississippian
89 Albert Mines Oil Shale	Syngenetic	Banded and disseminated in dolomitic shale	Albert Mines, N. B.	Albert	Mississippian
90 Albertite	Epigenetic	Inclusions in calcite veinlets	Near Scotsburn, Pictou Co., N. S.	River John	Mississippian
98 Windsor Limestone	Syngenetic	Disseminated in limestone	Port Hood Island, Nova Scotia	Windsor	Mississippian
101 Halifax Slate	Syngenetic	Disseminated in slate	Black River, near Wolfville, N. S.	Halifax	Ordovician
103 Halifax Slate	Syngenetic	Disseminated in	Near Grand Lake, Halifax, Co., N. S.	Halifax	Ordovician
106 Fortin Slate	Syngenetic	Disseminated in slate	Near Routherville, Quebec	Fortin	Devonian
107 Anthraxolite	Epigenetic	Associated with limestone and copper ore	Gagnon Brook, St-Denis township, Que.	Pohenegamook	Ordovician
109 Anthraxolite	Epigenetic	Inclusions in calcite in veinlets	Near Matane, Que.	Pohenegamook	Ordovician
112 Pine or Slave Point Dolomite	Syngenetic ?	Disseminated in dolomite	Phillips Minaker Well (A-25-d), near Fort Nelson, B. C.	Pine Point or Slave Point	Devonian
117 Impsonite	Epigenetic	Inclusions in calcite	Ile d'Orléans, Que.	--	Ordovician
118 Porcupine Ore	Epigenetic	Disseminated in gold and sulphide ore	McIntyre-Porcupine Mine, Timmins, Ont.	--	Precambrian
121 New Glasgow Oil Shale	Syngenetic	In shale bed overlying coal seam	Stellararton, N. S.	Stellararton	Pennsylvanian
127 Utica Oil Shale	Syngenetic	Disseminated in calcareous shale	Cap-Santé, Quebec	Utica	Ordovician
128 Sudbury-Anthraxolite	Epigenetic	Vein material, moderately high ash content	Chelmsford, Ont.	--	Precambrian

1/ A question mark indicates an element of doubt in the genetic designation. The McMurray oil sands are generally considered to be of secondary origin.

TABLE 2

Chemical Analyses of Samples

Sample Désignation	Chemical Analysis - % by weight		
	Carbonate	Organic Carbon	Sulphur
82 Thucholite		46.0	9.8
83 McMurray Oil Sands, Mildred Lake		16.0	Not determined
85 McMurray Oil Sands, Abasand Quarry		13.0	Not determined
87 Argillite	91.5	0.5	0.3
88 Carboniferous Fish Scales	49.5	1.2	2.0
89 Albert Mines Oil Shale	32.3	30.7	0.9
98 Windsor Limestone	97.2	0.2	0.02
101 Halifax Slate	17.7	0.3	0.2
103 Halifax Slate	6.3	1.1	0.2
106 Fortin Slate	24.3	0.7	0.2
112 Pine or Slave Point Dolomite	84.3	0.8	0.7
118 Porcupine Ore ^{1/}	89.3	0.1	0.1
121 New Glasgow Oil Shale	36.0	19.8	0.3
127 Utica Oil Shale	64.0	1.8	0.9
128 Sudbury Anthraxolite	2.7	65.8	0.1

^{1/} "High-graded" with respect to carbon.

niques from related fields; for example, techniques used in the separation of microfossils (9). The modifications introduced appear to have improved the existing methods of separation, as the ash contents of the organic isolates recorded in this report are, on the average, lower than those reported in the literature. As a general rule, no single technique is effective for the removal of organic matter of low ash content from the majority of samples, and a combination of at least two methods is usually required for most lithologic types. In planning the best procedure for a given sample it is helpful to first acquire a petrographic knowledge of the sample by thin section study. In this respect it is important to note the nature, particle size and distribution of the organic matter, as well as the relative amounts of calcareous, siliceous, and pyritic material. The texture and cementation should also be noted. With experience, the thin-section evaluation of the organic matter often provides a qualitative appreciation for its physical and chemical properties from a consideration of its relative absorption characteristics. The examination also indicates whether or not more than one petrographic organic component is present, and if so, the possibilities of rendering a separation.

Throughout this investigation emphasis has been placed on the recovery of the organic matter as a whole in an unfractionated state. For this reason, separation by mechanical means has been emphasized with the aid of acid treatment, thus making it possible to carry out the entire separation in an aqueous medium. For the most difficult separations hydrofluoric acid treatment is used, and this is followed by a mechanical separation to remove the insoluble fluorides. As a result of these restrictions, however, the yields of organic matter are rather low. Solvents are only employed when the organic matter is found to be almost completely soluble in a solvent that can be readily removed after the extraction.

The techniques used to isolate organic matter of a low ash content are: (I) heavy-liquid separation, (II) air-water flotation, and (III) a combined chemical and mechanical separation using hydrofluoric acid followed by ultrasonic agitation and slow settling.

I. Heavy-liquid Separation

This method is restricted to those samples which upon grinding contain particles of pure organic matter greater than 37 microns diameter (400 Tyler mesh). Removal of the fine particles is necessary to prevent coagulation and adherence of fine impure particles to coarser pure fractions. This method proved to be very satisfactory for the vein deposits, and for two of the organic-rich shales, the Albert and New Glasgow oil shales.

Since it is desirable to work with an aqueous medium in order to avoid organic contamination and partial fractionation through solution, a concentrated solution of zinc bromide is used as a heavy liquid. The zinc bromide solution is acidified with a 10% hydrochloric mixture during its preparation, to prevent the precipitation of zinc hydroxide. The chief advantage of the zinc bromide over the more commonly used zinc chloride is the much lower viscosity of the former; thus rapid, clearcut separations can be obtained.

The samples are first crushed by stages to the desired particle size, depending on the nature and distribution of the organic matter, and the fines are removed by wet-screening through a 400-mesh sieve and discarded. The sample is then acidified with dilute hydrochloric acid and thoroughly mixed with a large excess of the heavy-liquid medium in a beaker of appropriate size and allowed to separate. The light fraction or sample is removed from the surface by a suction arrangement provided with a trap. The concentrate is then re-separated using a zinc bromide medium of lower gravity adjusted to the particular sample by dilution with 10% hydrochloric acid. The sample is finally washed by centrifuging with 10% hydrochloric acid and then with hot distilled water.

In some cases the above procedure provides a sufficiently clean sample; however, depending on the distribution of the mineral matter with respect to the organic matter, it is sometimes necessary to regrind the sample and further refine it according to method III.

II. Air-water Flotation

This is a simple but very effective flotation method of preparing carbon concentrates from metamorphic rocks containing low concentrations of finely disseminated organic matter by merely submerging a sample of dried crushed rock in distilled water and applying a slight vacuum to the system. Since the organic matter from the metamorphic rocks is strongly hydrophobic, the finely divided material forms a stable system at the air-water interface. The flotation is further enhanced by the fact that because the organic matter possesses an internal surface the application of a slight vacuum causes the formation of bubbles at the surface of the particles; thus the particles are carried rapidly to the surface of the water. During this investigation the flotation method has been used to obtain concentrates of organic matter containing in the order of 10 to 15% ash from metamorphic rocks containing in some cases less than 1% organic carbon.

The concentrates can be further purified by recycling, but this process soon reaches a point of diminishing returns with respect to the yield of organic matter. It is most efficient to recycle only once or twice and then treat the concentrate with hydrofluoric acid according to method III. Using the combined techniques, the ash contents of a number of samples

were reduced below 1%; however, in most cases the final ash contents varied between 1 and 6%. Since the ash contents of the flotation concentrates are relatively low, difficulties are generally not encountered with insoluble fluorides when the concentrates are treated with hydrofluoric acid.

In detail, the procedure consists of first crushing the sample by stages to pass a 10-mesh sieve. A high percentage of the organic matter is released to the finer fractions rather early in the grinding process, and fine grinding of the entire sample only tends to inhibit the flotation process. Optimum grinding conditions, however, probably vary considerably for widely different lithologic types and rock textures. The sample is then dried at 105°C under vacuum for approximately one hour.

In preparing calcareous rocks for flotation, the sample is crushed to pea size and digested in dilute hydrochloric acid. The dried residue is then ready for flotation without further grinding.

After drying, the samples are divided into 400-gram lots and placed in one-litre beakers. Distilled water is added slowly while the sample is stirred to a paste, after which the beaker is completely filled with water and immediately placed in a vacuum desiccator under a slight vacuum. The carbon concentrate forms almost immediately at the surface, either as a foamy film or as a glossy slick. Following formation of the film it is desirable to release the vacuum to prevent loss of sample by sputtering. Since the film is highly surface active, it is removed by compressing it to one side of the beaker with a one-inch-diameter glass rod held in a horizontal position across the surface, after which the rod is rotated and the sample is gathered on the rod surface. The sample is washed from the surface of the rod to a clean beaker and recycled once or twice using the same procedure with the exception of the drying stage. Using this technique for collecting the film, a fairly complete separation is effected between the organic concentrate and the substrate containing the inorganic suspension. Following flotation, the sample is prepared for hydrofluoric treatment.

Yields from the flotation procedure averaged approximately 1% of the original carbon present in the sample; however, these low yields are more than offset by the advantages of the method. The only serious disadvantage is that the method appears to be restricted to metamorphic rocks.

III. Hydrofluoric acid-Ultrasonic-Settling Technique

The usefulness of the two previously described separation methods depends to a large extent on the nature of the sample and cannot apply to all occurrences; however, they have particular advantages and should be used, where possible, for the preparation of concentrates. In contrast, method III is much more time-consuming but has the distinct advantage that it can be applied to almost any specimen in effecting a separation provided the

organic matter in question is not seriously altered by the hydrofluoric acid. This method also provides larger yields, a fact that could be used to advantage if the sample were in short supply.

Briefly, the method consists of a hydrochloric and hydrofluoric acid treatment for the removal of carbonates, silicates and silica, followed by an ultrasonic agitation to disperse the insoluble fluorides; a procedure currently used for the preparation of clean microfossil mounts (9). This is followed by a differential settling procedure to separate organic matter and insoluble fluorides, and, finally, a second differential settling to separate organic matter and pyrite.

In detail, the samples are first ground to minus 100 mesh and treated overnight with excess hydrochloric acid. The acid residue is thoroughly washed with distilled water and recovered by centrifuging. Since most sedimentary rocks contain some soluble calcium, it is desirable to treat all samples, whether they are limestone or shale, with hydrochloric acid before the hydrofluoric acid treatment, in order to reduce the formation of fluorides.

The washed residue is then placed in Nalgene centrifuge tubes and after the addition of a few millilitres of isopropyl alcohol, 48% hydrofluoric acid is slowly added until the ratio of acid to sample exceeds 30. The mixture is then heated over a water bath at 70°C for approximately 4 hours with occasional stirring, whereupon it is centrifuged, the liquid decanted, and the residue treated with fresh acid using the same procedure. Finally, the sample is washed and recovered by centrifuging.

To remove the insoluble fluorides, the wet residue is divided into 2-gram lots and placed in 1-litre beakers. After the addition of 3 drops of laboratory detergent (Aquet), the beakers are filled with distilled water and agitated in an ultrasonic bath (average power output of 50 watts of 40 kc energy) for 1 to 2 minutes. The ultrasonic agitation breaks up the flocculated clusters of insoluble fluoride, and removes them from the surface of the organic matter. The fluorides are held in a state of dispersion while the organic matter and remaining coarse impurities settle out. The large excess of water is required to prevent the system from coagulating, in which event no separation will take place. A 2-to-3-day settling period is usually required for the first separation, depending somewhat on the particle size of the organic matter and the amount of insoluble fluoride present. Upon completion the suspended impurities are removed by suction. This procedure is repeated several times, including the ultrasonic agitation and the addition of detergent, until clear solutions are obtained at the end of the settling period. Since the settling time varies considerably, it is desirable to monitor each run to note progress. This is accomplished by microscopic examination of the dispersed phase, to observe the relative amounts of organic matter and insoluble fluoride present. Microscope mounts for this examination are prepared by smearing a drop of the solution on a slide and allowing it to dry.

Following completion of the above separation, the organic matter is again treated with hydrofluoric acid in the manner prescribed earlier, and once again the ultrasonic agitation and slow settling techniques are applied.

At this stage, the sample contains organic matter and impurities unaffected by the hydrofluoric acid such as pyrite and zircon. Pyrite is often present and can be very intimately dispersed in the organic matter; an association that usually arises from the original environment of deposition where the organic matter provides the reducing conditions necessary for the pyrite formation. During this investigation, an attempt was made to remove pyrite by means of nascent hydrogen, a technique prescribed by Himus and Basak (10) and modified by Forsman and Hunt (3). This technique proved unsuccessful in removing most of the pyrite, whereupon a differential settling technique was devised. This technique entails micronizing the organic concentrate in aqueous suspension in a rod mill for approximately 15 hours to further free the organic matter from the pyrite. A few drops of detergent and a large excess of water are added to this suspension, followed by a 2-minute agitation in the ultrasonic bath. The suspension is allowed to settle overnight and the pyrite and organic matter separate differentially; the organic matter remains in suspension. Several such treatments effect a satisfactory separation. For example, the sulphur content of the pyrite-organic concentrate from the Utica shale was reduced from approximately 28 to 3.7 percent.

As stated previously, many of the samples listed in Table 1 only required hand-picking for purification. The samples that were actually purified by one or more of the methods described above are those for which chemical analyses of the original samples are listed in Table 2, with the exception of samples 83 and 85 which were obtained by benzene extraction. This constitutes a total of 13 samples treated according to the methods described above. The ash contents of the purified samples are indicated in Table 3, and show that, with the exception of sample 87, the ash contents are remarkably low considering the concentration of carbon in the original samples. The average ash content of the 13 samples treated is approximately 4 percent. It should be noted that certain improvements in technique were incorporated during the course of the preparation work, so further reductions in ash and higher yields of organic matter could be expected in future work.

DETERMINATION OF PROPERTIES

Elemental Analyses

Microanalyses for carbon, hydrogen, nitrogen, sulphur and ash were performed by Micro-Tech Laboratories, Skokie, Illinois, on the samples listed in Table 1 in their purified state. The results are listed on a weight percent basis in Table 3. A correction was applied to the sulphur in cases where the pyrite content of a sample was significantly high. The oxygen was determined by difference. Table 3 also shows the carbon, hydrogen and oxygen contents calculated on an atom percent basis and free of nitrogen, sulphur, and ash. The samples are arranged in the order of increasing atom percent carbon.

Proximate Analyses

Volatile determinations were made according to ASTM Designation: D 271-58 (12); however, modifications were introduced because of limited amounts of sample. The standard method requires one gram of sample, which normally yields enough volatile matter to protect the sample from serious oxidation. When smaller samples were used it was found necessary to protect the sample in a nitrogen atmosphere. This was accomplished by first stripping the sample of adsorbed air under vacuum and then replacing it with nitrogen. In addition, the Fieldner furnace was flushed with nitrogen immediately before a run, and the hot crucible containing the sample was quenched in nitrogen at the end of the run. Under these conditions it was possible to reduce the sample size to 75-100 milligrams, and the heating time to four minutes, without altering the results ordinarily obtained with the standard method. The ash-free values for volatile matter are shown in Table 3.

Refractive Index

Since the majority of samples investigated absorb light strongly in the visible range, it was necessary to employ an indirect method for the determination of the refractive index. This method involves the measurement of the reflectance of vertically incident light from polished surfaces. Reflectance measurements in two media are required, and for purposes of this investigation air and water proved most suitable. The refractive index was calculated from the reflectance measurements by means of the following equation, derived from the Maxwell theory (13), which relates reflection, refraction, and absorption:

$$R = \frac{(n-n_0) + (nk)^2}{(n+n_0) + (nk)^2},$$

TABLE 3

Physical, Chemical and Optical Properties of Samples Arranged in the Order of Increasing Atom Percent Carbon
(The method used for purification of the samples is also indicated.)

Sample Designation	Elemental Analysis, Ash Free Weight %					Ash %	Volatile Matter % Ash Free	Pyrite % 2/	Method of Purification 3/	Elemental Analysis Ash, S, and N Free			Atomic Ratios				Density ^{4/} d ₄ ²⁵	Refractive Index, n _D ²⁵	Solubility in CS ₂ , %	Aromaticity, f _a
	C	H	N	S 1/	O by diff.					Atom %			H C	N C	S C	O C				
										C	H	O								
33 Ozokerite	85.9	14.1	-	-	-	-	97.8	-	HP	33.7	66.3	-	1.97	-	-	-	0.946	1.53	99.8	0.0
69 Asphaltic Ozokerite	87.1	12.5	0.2	0.1	0.1	-	90.3	-	HP	36.7	63.2	0.1	1.72	0.002	-	0.001	0.915	1.52	98.9	0.18
46 Liverite	82.9	11.2	2.5	1.9	1.5	0.6	94.3	-	HP	38.0	61.5	0.5	1.62	0.026	0.009	0.014	1.00	1.56	98.0	0.21
43 Ingramite	81.4	10.7	1.4	1.3	5.2	-	88.7	-	HP	38.1	60.1	1.8	1.58	0.014	0.006	0.048	1.028	1.54	6.1	0.22
36 Wurtzilite	81.4	10.9	3.4	2.2	2.1	0.3	91.8	-	HP	38.2	61.1	0.3	1.61	0.036	0.010	0.019	1.022	1.56	4.8	0.20
89 Albert Mines Oil Shale	82.1	10.7	1.2	1.4	4.6	1.0	93.0	-	(1), (3)	38.4	60.0	1.6	1.56	0.013	0.006	0.042	1.006	1.55	3.1	0.29
121 New Glasgow Oil Shale	85.7	11.4	0.7	0.4	1.8	0.6	92.8	-	(1), (3)	38.4	61.0	0.6	1.60	0.007	0.002	0.016	0.984	1.55	-	0.22
42 Tabbyite	84.6	10.8	1.7	0.6	2.3	-	90.2	-	HP	39.1	60.1	0.8	1.53	0.017	0.003	0.020	1.008	1.58	100.0	0.28
85 McMurray Oil Sands	82.9	10.3	0.5	5.4	0.9	0.5	88.9	-	Benzene extraction	40.1	59.6	0.3	1.49	0.005	0.024	0.008	1.027	1.60	100.0	0.33
45 Gilsonite	85.5	10.5	2.7	0.4	0.9	0.2	85.5	-	HP	40.4	59.3	0.3	1.47	0.027	0.002	0.008	1.037	1.60	99.2	0.30
83 McMurray Oil Sands	83.0	10.0	0.5	5.0	1.5	-	90.9	-	Benzene extraction	40.6	58.8	0.6	1.45	0.006	0.023	0.014	1.011	1.59	100.0	0.39
34 Albertite	84.1	9.4	2.0	0.3	4.2	-	69.3	-	HP	42.1	56.3	1.6	1.34	0.020	0.001	0.037	1.078	1.65	1.8	0.41
35 "	82.8	8.7	0.8	0.3	7.4	-	62.2	-	HP	43.0	54.2	2.8	1.26	0.008	0.001	0.067	1.122	1.70	6.0	0.47
98 Windsor Limestone	71.1	6.3	2.2	4.1	16.3	6.0	54.6	2.0	(3)	44.8	47.5	7.7	1.06	0.027	0.022	0.172	1.38	1.70	-	-
44 Grahamite	81.2	7.7	1.7	1.4	8.0	2.3	57.5	-	HP	45.3	51.3	3.4	1.14	0.018	0.006	0.074	1.17	1.69	97.0	0.56
49 "	82.3	8.1	1.6	6.4	1.6	-	61.4	-	HP	45.6	53.8	0.6	1.18	0.017	0.029	0.015	1.155	1.70	95.6	0.55
127 Utica Oil Shale	81.5	7.4	1.5	0.2	9.4	6.5	51.4	8.1	(3)	46.0	50.0	4.0	1.09	0.016	0.001	0.087	1.17	1.72	-	0.60
77 Albertite	86.6	8.0	1.1	2.5	1.8	0.5	48.2	-	HP	47.0	52.2	0.8	1.11	0.011	0.018	0.016	1.174	1.74	40.3	0.57
73 "	87.4	7.9	1.2	1.6	1.9	0.4	50.2	-	HP	47.6	51.5	0.9	1.08	0.012	0.007	0.016	1.136	1.70	28.9	0.61
88 Carboniferous Fish Scales	79.5	6.6	1.1	4.4	8.4	4.1	51.4	2.1	(1)	48.1	48.0	3.9	0.99	0.012	0.021	0.079	1.27	-	-	0.61
90 Albertite	91.9	7.9	-	0.2	-	0.6	45.7	-	(1)	49.3	50.7	-	1.03	-	0.001	-	1.134	1.73	9.3	0.65
78 Impsonite	81.3	5.8	0.4	2.0	10.5	1.0	33.9	-	HP	51.3	43.6	5.1	0.86	0.004	0.009	0.097	1.31	1.82	2.8	0.72
82 Thucholite	74.4	4.6	0.3	0.7	20.0	3.0	32.8	-	HP, (1)	51.7	37.9	10.4	0.74	0.003	0.004	0.202	1.55	1.81	1.2	-
79 Impsonite	88.8	5.5	0.7	1.1	3.9	2.6	24.9	1.1	HP	56.3	41.9	1.8	0.74	0.007	0.005	0.033	1.27	1.83	3.2	0.86
117 "	90.2	5.2	1.3	0.6	2.7	0.3	24.4	-	(1)	58.3	40.3	1.4	0.69	0.012	0.002	0.023	1.27	1.88	2.3	0.88
50 "	90.1	5.1	0.5	2.2	4.3	2.4	26.7	-	HCl, HP	58.4	39.5	2.1	0.68	0.005	-	0.036	1.32	1.84	-	0.85
51 "	88.9	4.8	1.3	0.4	4.6	0.3	20.5	-	HP	59.2	38.5	2.3	0.65	0.013	0.002	0.039	1.349	1.92	1.1	0.87
53 "	89.1	4.8	1.3	0.9	3.9	0.3	16.0	-	HP	59.6	38.5	1.9	0.65	0.013	0.004	0.033	1.344	1.95	1.3	0.87
112 Pine or Slave Point Dolomite	73.4	2.5	0.8	6.0	17.3	7.2	24.9	8.1	(3)	63.0	25.9	11.1	0.41	0.009	0.031	0.177	1.63	-	-	-
52 Anthraxolite	91.2	3.4	0.7	0.3	4.4	5.6	9.0	-	HP	67.6	29.9	2.5	0.45	0.007	0.001	0.036	1.45	1.99	<0.5	0.95
109 "	91.2	3.1	1.0	0.3	4.4	2.4	9.9	-	(1)	69.5	28.0	2.5	0.41	0.009	0.001	0.036	1.46	2.01	0.5	1.0
107 "	92.6	3.2	0.8	0.3	3.1	0.7	6.8	-	(1)	69.6	28.6	1.8	0.41	0.007	0.001	0.025	1.50	1.98	<1.0	1.0
54 "	91.7	3.0	0.9	0.5	3.9	0.2	6.3	-	HP	70.5	27.3	2.2	0.39	0.008	0.002	0.032	1.515	2.00	-	0.98
106 Fortin Slate	91.4	1.8	1.0	1.3	4.5	2.3	-	-	(2), (3)	78.9	18.2	2.9	0.24	0.009	0.005	0.037	1.66	-	-	1.0
118 Porcupine Ore	93.1	1.2	0.4	0.9	4.4	4.4	6.1	5.3	(2), (3)	84.2	12.8	3.0	0.15	0.004	0.004	0.035	1.87	-	-	1.0
101 Halifax Slate	95.2	1.3	0.6	0.2	2.7	0.9	7.6	-	(2), (3)	84.5	13.7	1.8	0.16	0.005	0.001	0.021	1.92	-	-	1.0
128 Sudbury Anthraxolite	94.1	1.1	0.7	0.4	3.7	1.1	6.5	-	(1)	85.5	11.9	2.6	0.14	0.006	0.002	0.029	1.96	2.06	0.1	1.0
103 Halifax Slate	96.8	0.9	-	0.5	1.8	3.8	-	-	(2), (3)	88.9	9.9	1.2	0.11	-	0.002	0.014	2.06	-	-	1.0
87 Argillite	92.8	0.7	-	2.6	3.9	13.0	3.7	10.3	(2), (3)	89.3	7.9	2.8	0.09	-	0.010	0.032	2.3	-	-	1.0
6/ Ceylon Graphite	99.1	0.5	<0.1	0.2	0.1	0.3	-	-	-	94.2	5.7	0.1	-	-	-	-	2.25	-	-	-

1/ Sulphur corrected for presence of pyrite.

2/ Calculated from spectroscopic analysis for Fe, assuming all Fe present as pyrite.

3/ HP - Hand-picked; (1), (2), (3) - Indicates methods of purification described under section on preparation of samples.

4/ Density corrected for mineral matter, using the spectrographic analysis as a guide to the nature of the mineral matter present.

5/ Calculated on a sulphur- and ash-free basis.

6/ Elemental analysis of graphite after Erdman and Ramsey (11).

where

- R = the fraction of incident light which is reflected,
- n = the index of refraction of the material under investigation,
- k = the index of absorption of the material, and
- n_0 = the index of refraction of the medium (air and water).

The apparatus and technique employed have been previously described by King, Nandi and Montgomery (14).

The preparation of polished surfaces for reflectance measurements represents a critical step in the procedure, and the wide variety of samples necessitated the use of a number of preparation techniques. For solid materials that became plastic at temperatures below 100°C, surfaces were prepared by squeezing 25 to 30 milligrams of the sample between clean microscope slides with the aid of a handpress. Upon cooling, further pressure was applied and the sample generally separated from one of the glass slides. Surfaces of optical quality were prepared in this manner.

The majority of samples would not become sufficiently plastic at moderate temperatures for preparation in the above manner, and it became necessary to use higher pressures provided by a metallographic mounting press. A flat surface was ground on the specimen and placed face down on the bottom piston of the mould. The specimen was then covered with Lucite powder and mounted in the conventional manner, at a temperature of 120°C and pressure of 8,000 psi. After cooling, the bottom piston was removed and a clean microscope cover glass was inserted between the piston and the specimen, after which the assembly was reheated and pressed. This resulted in an intimate contact between the flat surface of the specimen and the glass. The embedded cover glass was then shattered by a thermal shock induced by cooling to 0°C and sudden warming to room temperature. It was found desirable to limit the size of the specimens to 1 to 5 millimetres in diameter, to minimize strain and distortion after release of the pressure. A number of grains can be mounted simultaneously.

For the highly polymerized specimens, such as the impsontites and anthraxolites, the grains were mounted in plastic and lap-polished on parachute and Selvyt cloths with powdered alumina.

Finely powdered specimens were reconstituted by means of high pressures before the appropriate polishing procedures were applied. Adequate surfaces for some of the very high rank powdered specimens could not be prepared.

In the case of the semi-liquid specimens, reflectance measurements in air were made from the liquid surface and the refractive indices were calculated from the measurements in the one medium, assuming K was equal to zero. This was justified by the lower absorption indices of the liquids.

The quality of the polished surfaces prepared by the above methods was initially difficult to evaluate by means of the reflecting microscope, so a reflecting interference microscope was employed which effectively produced highly accurate surface contours of the polished specimens. The best areas for reflectance measurements were chosen in this manner. It was later found that an adequate assessment of the surface could be made with the reflecting microscope, by throwing the specimen slightly out of focus and noting the degree of homogeneity in the field. A uniform field was indicative of an optical surface, while variations in light intensity across the field indicated imperfections in the surface. Thus, the reflecting interference microscope proved to be useful but not essential.

Anisotropism was noted in the impsonites and anthraxolites, either as a uniform extinction across the entire field or as randomly oriented anisotropic crystals of very fine particle size. Both situations complicated the reflectance measurements. Measurements on the crystalline varieties represent an average value for the refractive indices, since the crystals are randomly oriented and many are present for a given view at low magnification. The ordinary and extraordinary rays could not be considered separately because of the fine nature of the crystals.

For samples showing a uniform extinction, the refractive index of the ordinary ray was obtained by assuming a uniaxial negative indicatrix. Since the reflectance depends on the orientation of the particles in the mount, it was not practical to measure both the maximum and minimum indices, as this would necessitate measurements on many particles in order to locate one near the correct orientation. In the case of coal the orientation problem is not so difficult, as the indicatrix is oriented with respect to the bedding. Van Krevelen and Schuyer (15) have shown that coal has a uniaxial negative birefringence which arises from the orientation of aromatic structural units which are themselves anisotropic. It seems reasonable to assume that the anisotropy exhibited by the samples under investigation arises from a similar type of preferred orientation of aromatic nuclei having uniaxial negative birefringence, that is, the higher index represents the ordinary ray. Since the ordinary ray can be determined for any orientation of the particles, the maximum reflectance reading during rotation of the microscope stage should represent the ordinary ray if the assumption of a negative indicatrix is correct.

The refractive index data are tabulated in Table 3. Measurements were made at 25°C temperature, with maximum light intensity at 589 millimicrons.

Density

Density measurements were made by a semimicro pycnometric method in water at 25°C. The method was first described by Hock (16) to determine the density of coal-tar pitch and was modified in this laboratory (17) for finely powdered materials. The pycnometer consists of a 6-millimetre glass tube, 18 millimetres in length and closed at one end. The open end or top of the tube has a finely ground surface and during a determination it is sealed with microscope cover glass. When the tube is filled with water the surface tension holds the cover glass firmly in position, and a very slight excess or deficiency of water is visually apparent at the interface of the cover and tube.

In order to obtain the true density of solid materials having an internal surface, the samples are ground and suspended in water under water-pump vacuum pressure. The suspension is initially stirred magnetically to remove air bubbles adhering to the particle surfaces, and to keep the sample submerged. The submerged particles are kept under vacuum in water for 6-8 days to enable the water to completely penetrate the pores. The powdered material is packed in the bottom of the pycnometer by centrifuging.

Duplicate determinations on a 25-milligram sample agree within one percent, and samples in the 100-milligram range usually agree to 0.1 percent. The density results are shown in Table 3.

Solubility in Carbon Disulphide

Solubilities in carbon disulphide were determined at 25°C according to ASTM Designation: D 4 - 52 (18), except that smaller samples were used and the Gooch crucible and asbestos mat were replaced with a Selas porcelain filtering crucible having a medium porous bottom. The results are tabulated in Table 3.

Infrared Analyses ^{1/}

The infrared spectra were measured on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics. Several methods of sample preparation were required to measure the spectra because of the wide variety of materials being studied, which ranged from semi-fluids to graphitic solids. Since the main aim was to obtain comparable spectra representing all samples in their entirety and acquire as much quantitative data as possible, the method suitable to the largest number of samples was used as extensively as possible. The potassium bromide pellet technique provided good spectra on all but six of these materials. Pellet spectra were also obtained on two of these six and supplied cross-reference data for the other

^{1/} Miss F. E. Goodspeed was responsible for the infrared aspect of this study.

methods employed. The following three methods were used:

(1) Potassium Bromide Pellets

Harshaw infrared-quality potassium bromide (KBr) was used throughout. Pellet mixtures of sample concentrations ranging from 0.01 to 1.0 percent by weight in KBr were prepared to provide quantitative data on absorption bands of widely varying strengths. Where several concentrations were required for a given sample, the most concentrated mixture was prepared in sufficient quantity to make one pellet and supply the additional amounts needed to prepare the desired dilutions with additional KBr. Small amounts of benzene were added to facilitate the mixing of the samples with KBr, especially where the samples were partly or wholly soluble. The mixture was ground to dryness in an agate mortar and the remaining traces of benzene were removed by heating in an oven at 105°C for 1/2 to 1 hour and evacuating in a desiccator for 1/2 to 1 hour. The particle size of all the solid substances was reduced in a vibration ball mill as required to produce good spectra. The pellet mixtures of insoluble samples were ground dry in an agate mortar and micronized for two minutes in the vibration mill before pressing. Each pellet weighed 0.5 gram and was pressed at 12,000 psi under vacuum. Under these conditions, pellets of a standard thickness of 1.0 millimetre were obtained.

(2) Films

Films were used for the fluid materials and were prepared by spreading the sample on a sodium chloride plate. These provided qualitative spectra from 2 to 15 microns.

(3) Solutions

Carbon tetrachloride solutions of the soluble materials were used to obtain quantitative data in the 3- and 7- micron regions. Carbon disulphide solutions similarly provided data in the 11 to 15 micron range, with equivalent solvent in the reference beam for compensation. A 0.5-mm cell was used for all solution measurements.

The quantitative data on all samples was reported as absorptivities:

$$a = \frac{A}{c \cdot b},$$

where a is absorptivity,

A is absorbance (optical density),

c is concentration in grams/litre, and

b is cell thickness in centimetres.

The density value of 2.75 was used for KBr in the conversion of concentrations from percent by weight to grams per litre. The reproducibility of the quantitative data from KBr pellet spectra was verified for all samples.

Reference data were obtained on over fifty pure high molecular weight hydrocarbon solids: 25 of these were entirely, or predominantly, saturated compounds from the American Petroleum Institute Research Project 42, and 32 were commercially available aromatic compounds. These data for specific absorption bands were used in conjunction with the peak height absorptivities of the samples studied, to determine the fraction of the total carbon present in a specific structural group.

Absorptivity values for the characteristic bands are shown in Table 4. The values for background absorption at 5 microns are representative of the whole material. All the other absorptivities are corrected to an ash-free basis since they represent the organic content and negligible inorganic absorption would occur at these wavelengths. This is in agreement with the other physical property data presented in Table 3, with which the infrared data are compared.

The absorption band absorptivities were measured from baselines equivalent to the background of the pellet at the designated wavelength, or a point which remained comparable throughout all spectra. The specific baselines chosen were:

- 3.42 μ peak height - background line from 2.75-4.50 μ
- 7.27 μ " " - " absorption at 7.1-7.2 μ
- 11.0-14.0 μ total absorption - background line from approximately 10.5-11.0 to 14.0-14.5 μ , as shown in Figure 1
- 13.9 μ peak height - baseline was dependent on the other absorption in the 11.0 to 14.0 μ range, as shown in Figure 1

Since the absorption attributed to aromatic CH in the 11 to 14 micron region consisted of very broad rather than sharp bands, a measurement characteristic of the whole 11.0 to 14.0 micron range was made. This measurement was the sum of the absorptivities at 30 points calculated from the baseline defined above at every 0.1 micron. Allowance was made for the absorption of the paraffinic methylene at 13.9 microns that occurred in some spectra. In Figure 1, the spectrum of albertite 73, the thirty absorbances measured are denoted by the vertical lines.

TABLE 4
Infrared Spectral Data

Sample Designation	Absorptivity, a		Aliphatic Carbon	
	fCH	fC	fCH	fC

Sample Designation	Absorptivity, a					Aliphatic Carbon			
	3.42 μ	7.27 μ	13.9 μ	11-14 μ	5 μ	f _{CH₂}	f _{CH₃}	f _{C_p} /f _{CH₂}	f _a + f _{CH₂} + f _{CH₃}
33 Ozokerite	2.32	0.055	0.159(s)	-	-	0.820	0.051	0.92	0.87
69 Asphaltic Ozokerite	2.17(s)	0.110(s)	0.076(s)	-	-	0.612	0.067	0.57	0.86
46 Liverite	1.28	0.140	0.015	0.27	-	0.476	0.136	0.09	0.82
43 Ingramite	1.02	0.082	0.055	0.20	0.03	0.378	0.081	0.43	0.68
36 Wurtzilite	0.99	0.083	0.036	0.36	0.03	0.369	0.086	0.29	0.66
89 Albert Oil Shale	1.23	0.053	0.067	0.27	0.03	0.459	0.052	0.43	0.83
121 New Glasgow Oil Shale	-	-	0.073	-	-	-	-	(high)	-
42 Tabbyite	1.33(s)	0.157	0.003(s)	0.34	0.02	0.386	0.107	0.07	0.77
35 McMurray Oil Sands	1.30(s)	0.144(s)	0.012(s)	0.65(s)	-	0.383	0.093	0.15	0.81
45 Gilsonite	1.20(s)	0.157(s)	0.008	0.42	0.02	0.340	0.098	0.06	0.74
83 McMurray Oil Sands	1.30(s)	0.148(s)	0.014(s)	0.71(s)	-	0.382	0.095	0.17	0.87
34 Albertite	0.72	0.090	0.031	0.52	0.14	0.265	0.086	0.33	0.76
35 "	0.79	0.065	0.030	0.55	0.20	0.290	0.063	0.29	0.82
98 Windsor Limestone	0.39	0.043	-	0.44	0.27	0.168	0.048	-	-
44 Grahamite	0.81	0.100	0.010	0.65	0.05	0.306	0.099	0.10	0.97
49 "	0.81	0.098	0.012	0.98	0.05	0.301	0.095	0.11	0.95
127 Utica Oil Shale	0.67	0.079	0.019	0.82	0.20	0.252	0.077	0.22	0.93
77 Albertite	0.72	0.085	0.011	1.17	0.09	0.254	0.079	0.12	0.92
73 "	0.77	0.085	0.018	1.13	0.08	0.270	0.078	0.19	0.96
88 Carboniferous Fish Scales	0.36	0.050	-	0.63	0.25	0.138	0.053	-	0.80
90 Albertite	0.51	0.042	0.020	1.25	0.19	0.170	0.037	0.31	0.86
78 Impsonite	0.49	0.076	0.008	1.36	0.09	0.185	0.075	0.12	0.98
82 Thucholite	-	-	-	-	0.79	-	-	-	-
79 Impsonite	0.40	0.065	Trace	1.92	0.21	0.139	0.069	-	1.07
117 "	0.31	0.040	-	1.33	0.23	0.107	0.036	-	1.02
50 "	0.15	(0.020)	-	1.70	0.56	0.051	0.018	-	0.92
51 "	0.22	0.046	-	2.04	0.35	0.076	0.042	-	0.99
53 "	0.22	0.058	-	2.18	0.13	0.076	0.052	-	1.00
112 Pine or Slave Point Dolomite	-	-	-	-	0.74	-	-	-	-
52 Anthraxolite	-	-	-	2.29	1.0	-	-	-	-
109 "	-	-	-	2.74	0.80	-	-	-	-
107 "	-	-	-	2.79	1.8	-	-	-	-
54 "	-	-	-	2.86	2.5	-	-	-	-
106 Fortin Slate	-	-	-	-	8.4	-	-	-	-
118 Porcupine Ore	-	-	-	-	9.7	-	-	-	-
101 Halifax Slate	-	-	-	-	14.0	-	-	-	-
128 Sudbury Anthraxolite	-	-	-	-	1.2	-	-	-	-
103 Halifax Slate	-	-	-	-	20.0	-	-	-	-
87 Argillite	-	-	-	-	11.2	-	-	-	-

(s) Solution data.

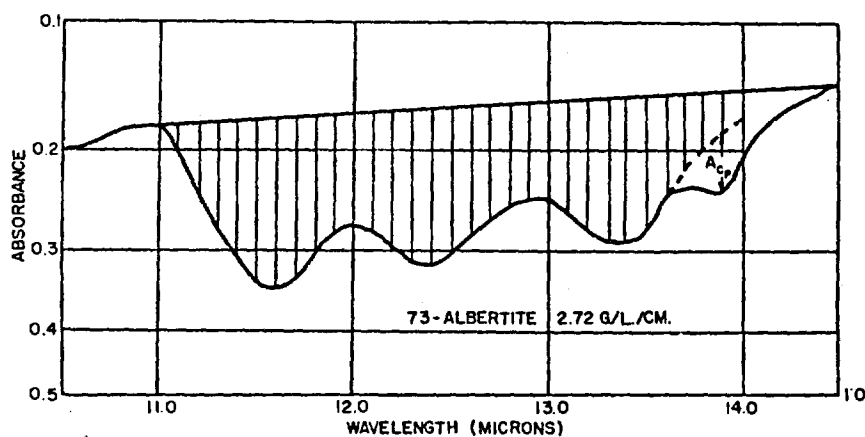


Figure 1 - The measurement of total absorption at 11-14 microns. Vertical lines represent the individual measurements totalled to give absorptivity, a . The absorption at 13.9 microns was calculated separately.

Aromaticity

Aromaticity of a hydrocarbon is defined as the aromatic carbon fraction: $f_a = C_a / C$, and is a highly desirable structural parameter for materials such as those under study. Van Krevelen and Schuyer (19) developed a method whereby aromaticity of hydrocarbons can be determined graphically from the elemental composition and the molar volume per carbon atom. The method is also applicable to organic substances containing oxygen, nitrogen and sulphur in addition to carbon and hydrogen, provided the necessary corrections are applied. The corrections constitute the transformation of a substance containing "foreign atoms": oxygen, nitrogen, and sulphur, to a hypothetical hydrocarbon of identical carbon skeleton. This procedure requires certain assumptions regarding the mode of occurrence of the foreign atoms. It is also maintained that the densimetric system holds for mixed aromatic-paraffinic and for mixed aromatic-naphthenic hydrocarbons, provided the aromaticity is greater than 0.25.

For many of the materials under consideration, it appears that the graphical densimetric method is applicable; however, a number of samples are not ideally suited in that those high in hydrogen probably have an aromaticity slightly below the 0.25 limit set by van Krevelen, and the impsonites and anthraxolites at the high carbon end of the suite are not completely amorphous. Furthermore, direct oxygen determinations and functional group data are not available for the accurate correction of foreign atoms. Consequently, the aromaticities were calculated on the basis of the assumptions that van Krevelen (19) used for coal; a procedure that is probably justifiable for the samples of low foreign atom content. Aromaticities are not reported for samples of exceptionally high foreign atom content.

Values for the reduced molar volume per carbon atom, corrected for foreign atoms, were obtained by the following equations:

$$\left[\frac{M_c}{d} \right]_{\text{exp.}} = \frac{1}{d} \left(12.010 + 1.008 \frac{H}{C} + 16.000 \frac{O}{C} + 14.008 \frac{N}{C} + 32.064 \frac{S}{C} \right)$$

where

M_c = the reduced molecular weight per carbon atom,

d = experimental density, and

H/C , O/C , etc. = atomic ratios.

$$\left[\frac{M_c}{d} \right]_{\text{corr.}} = \left[\frac{M_c}{d} \right]_{\text{exp.}} - \left(8.1 \frac{O}{C} + 6.4 \frac{N}{C} + 12.4 \frac{S}{C} \right).$$

Using the values for (M_c/d) corr. and the H/C atomic ratios, values for aromaticities are obtained graphically using van Krevelen's chart (19). The results are tabulated in Table 3.

Using the Montgomery-Boyd structural group analysis (20), values for f_a were also obtained on three samples from the 0.2 f_a range on which molecular weight determinations were available. These results confirm those from the graphical densimetric method.

1/ The experimental values in Table 3 for the refractive index and density of ozokerite are apparently high because of its crystalline nature, so for purposes of this report it is represented in the diagrams by the limiting values of these properties for paraffins. The experimental values for the asphaltic ozokerite further justify this conclusion. The aromaticity for ozokerite was calculated on the basis of the limiting values.

DISCUSSION OF RESULTS

An examination of the elemental analyses in Table 3 reveals a wide variation in the carbon, hydrogen and oxygen contents. It is, however, difficult to ascertain, in the data, any logical arrangement that might conform to the unique and varied properties of the suite of samples and thus serve as a basis for a highly definitive classification. Elemental analyses are not utilized in the Abraham classification (1) other than to differentiate the asphaltic and non-asphaltic pyrobitumens on the basis of oxygen content. On the other hand, coal can be successfully classified using elemental analyses on the weight percent basis, since the distribution of carbon, hydrogen and oxygen shows a fairly systematic pattern with respect to metamorphic development, as well as to other properties.

On the atom percent basis the elemental analyses can be utilized as classification parameters, and, as will be shown later in this discussion, by employing additional properties the classification can be rendered quite specific. Hoekstra and Fuchs (21) have recently illustrated the use of atom percent carbon, hydrogen and oxygen on a tri-axial diagram for the classification of carbonaceous materials. These illustrations are similar to the well known atomic H/C and O/C plots of van Krevelen (22) for the coalification series.

In addition to the use of elemental data on the atom percent basis for classification purposes, such data carry structural significance and depict a more fundamental picture when related to other properties which in turn can provide a clearer insight into some of the chemical and geological problems. In particular, the atom percent carbon is useful in conjunction with other properties to indicate the development tracks of the primary and secondary organic matter. The tracks for primary organic matter develop progressively, in response to metamorphic influence, in the direction of increasing carbon. The course of the development tracks for the secondary organic matter is influenced by fractionation in addition to the metamorphic control, and compositional and property changes arise from processes of selection and concentration of organic fractions from the primary organic matter. These problems are developed more fully later in the report.

Density and Experimental Molar Volume

The relation of density and atom percent carbon is shown in Figure 2, and the curves appear to indicate a number of important structural variations. The main curve extending from 33 to 100 atom percent carbon is defined by material of relatively low oxygen content; hence structural changes are not masked by varying concentrations of the heavy oxygen atom. In terms of the number of carbon atoms per 100 atoms of carbon, hydrogen and oxygen, the density increases at a decreasing rate from 33 to approximately 44-48 atom percent carbon, at which point the rate of increase becomes constant to approximately

70-75 atom percent carbon. Beyond the transition stage of 70-75 atom percent carbon, the curve is not so clearly defined because of insufficient data; nevertheless, it is clear that the density increases quite abruptly beyond 80 atom percent carbon, reaches a point of inflection around 85 atom percent carbon, and continues to increase at a decreasing rate to crystalline graphite. Sample 87 is possibly in error because of its high ash content.

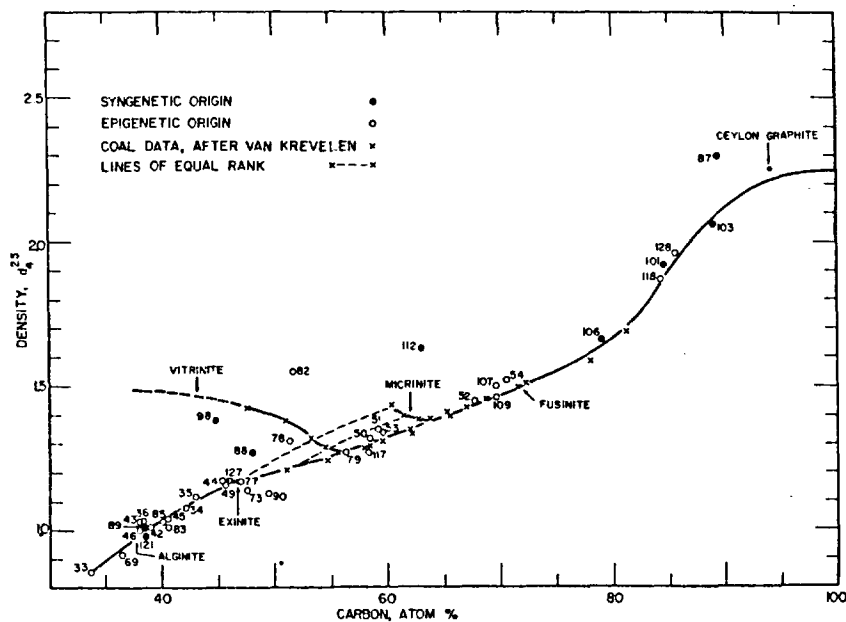


Figure 2 - Relation of density to atom percent carbon for the primary and secondary samples, including the coal macerals.

The increase in density between 33 and 70-75 atom percent carbon is probably due to ring formation. The initial high slope between 33 and 44-48 carbon atom percent is determined in part by a rapid increase in aromaticity as indicated in Figure 4, as well as by the presence of naphthenic rings (Table 5) which increase the density very rapidly with respect to loss of hydrogen atoms. The changing slope can be interpreted as the result of the change in the relative distribution of the two ring types.

The relatively constant rate of density increase (Figure 2) between the 44 and 75 atom percent carbon regions suggests a complex but ordered relation between the various factors affecting the curve: the relative distribution of paraffinic, naphthenic and aromatic types; the degree of ring fusion; the degree of stacking between aromatic nuclei; and the degree of polymerization. However, aromatization and aromatic ring fusion probably dominate the relation, inasmuch as the slope changes in the region

of 70-75 atom percent carbon, where the aromaticity becomes essentially equal to 1.0 (Figure 4).

The rapid increase in density beyond 80 atom percent carbon can be attributed to increased order and packing of the carbon atoms, leading to crystalline graphite formation in the area of 90 to 92 atom percent carbon. This view has been substantiated by X-ray evidence on coal (23).

Coal maceral data from van Krevelen (24)(25) have been added to Figure 2 for comparison purposes. The low rank vitrinites and micrinites form branches to the main curve because of their high oxygen contents, but as oxygen is eliminated through metamorphism these macerals pass through a minimum density and then blend with the main curve. These maceral data do not cover the lowest rank coals; however, it is well known that the low rank coals and peats extend into an even higher density range (26). The exinite and fusinite data conform to the main curve and do not form a branch for the range of rank covered. Sample 121, which is a sample of carboniferous algae resembling botryococcus brauni, also falls on the main curve at an even lower carbon content than the exinite. This material occurs in a basin containing coal of high volatile A bituminous rank equivalent to an atom percent carbon content of 55. Lines of equal rank can be obtained by joining macerals obtained from the same coal. It becomes clear that the individual rates of response of the various macerals to metamorphism are very different, especially for the low rank coal.

As will be seen later in terms of atom percent carbon, hydrogen and oxygen (see Figure 16), the vitrinite branch does not coincide exactly with the main track at low ranks, and the vitrinite does not join the main track until approximately 60 atom percent carbon. Both variations result from slight differences in oxygen content which apparently fall within the limits of accuracy of the density measurements.

The vitrinite and micrinite branches suggest that the high oxygen kerabitumen samples that do not fall on the main curve might basically be coal-like; consequently, their respective metamorphic tracks might be roughly deduced from the tracks of the macerals, but additional data and basic structural information are necessary to develop a conclusive argument in this regard.

In Figure 3 the experimental molar volume per carbon atom is plotted against atom percent carbon. Since the molecular weight of most of the samples is unknown, it is first necessary to calculate the reduced molecular weight from the elemental analysis, that is, the molecular weight per atom of carbon (M_c) previously mentioned in the method for determining aromaticity. The volume shows a decrease with respect to composition over the entire range and, like the density relationship, changes rate at 44-48 and 70-75 atom percent carbon as a result of structural reorganizations. The

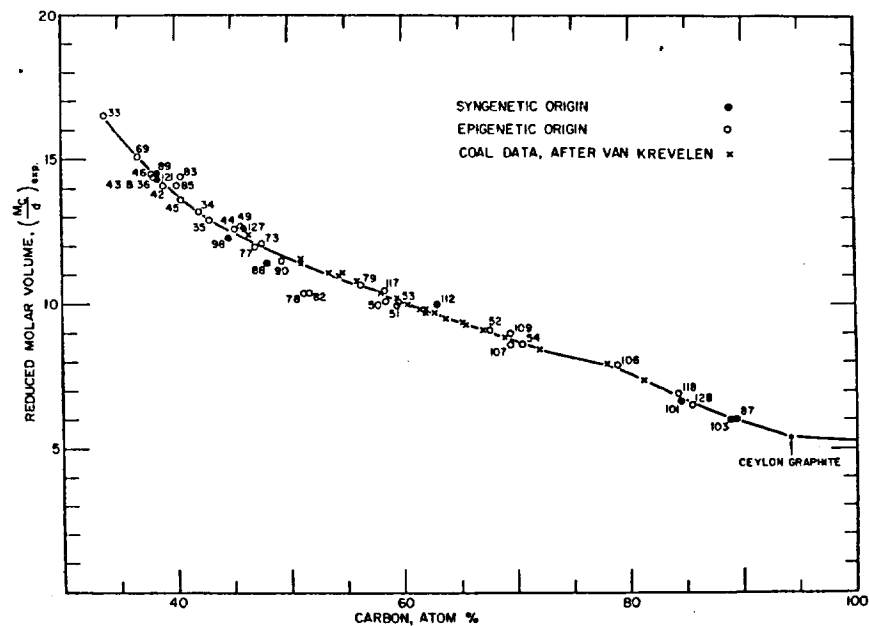


Figure 3 - Relation of experimental molar volume per carbon atom to atom percent carbon for the primary and secondary samples, including the coal macerals.

branch curves in the density plot, resulting from high oxygen content, are not evident in the molar volume plot, indicating that the oxygen groups present are, on the average, of such a type as to have made a similar atomic contribution as did hydrogen at the same atom percent carbon values. Samples 78 and 82 show an abnormal shrinkage where possibly the predominant oxygen type present is different from that of the average of the neighbouring samples. For sample 82, a thucholite, this might be a result of its association with uranium.

Aromaticity and the Ring Condensation Index

The relation of atom percent carbon to aromaticity is shown in Figure 4. The aromaticity increases constantly to approximately 44-48 atom percent carbon, at which point the rate begins to decrease. The aromaticity becomes equal to 1.0 in the region of 70-75 atom percent carbon. These transition areas, as previously pointed out, appear to indicate structural reorganizations.

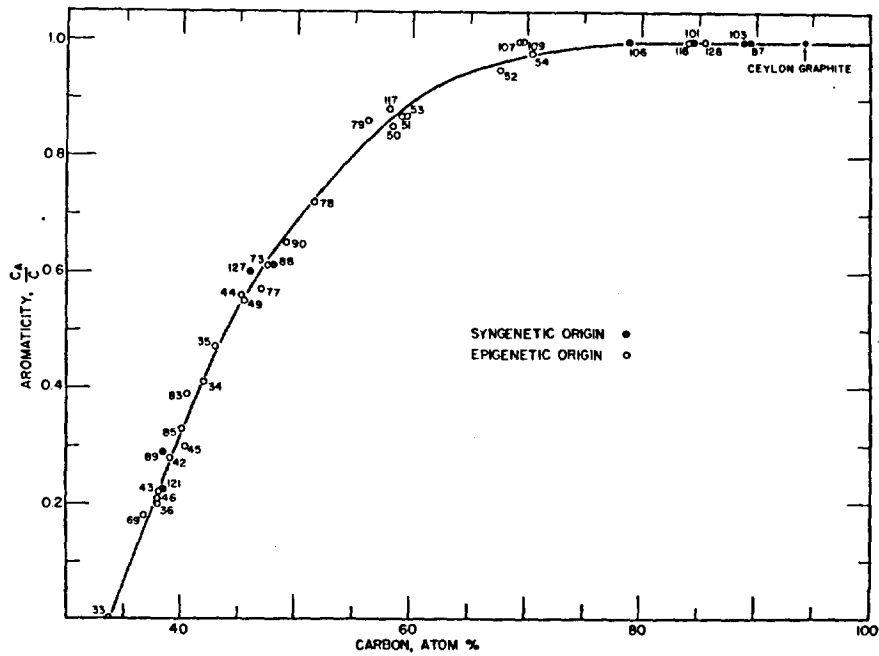


Figure 4 - Relation of aromaticity to atom percent carbon for primary and secondary samples.

A more fundamental relation between the elemental analysis and aromaticity was utilized by van Krevelen (27) through the following relation for hydrocarbon molecules possessing only aromatic unsaturation:

$$f_a = -\frac{H}{C} + 2 - \frac{2(R-1)}{C},$$

where

$\frac{2(R-1)}{C}$ = the "ring condensation index",

H/C = the atomic ratio,

R = the number of rings per structural unit,

C = the number of carbons per structural unit, and

f_a = the aromaticity.

The ring condensation index accounts for both aromatic and naphthenic rings whether fused or non-fused, and varies between zero for benzene and one for graphite. (See Appendix for further qualification.)

The above equation has been expressed graphically in Figure 5, in which aromaticity has been plotted against the H/C ratios and arbitrary lines of constant $2(R-1)/C$ have been inserted.

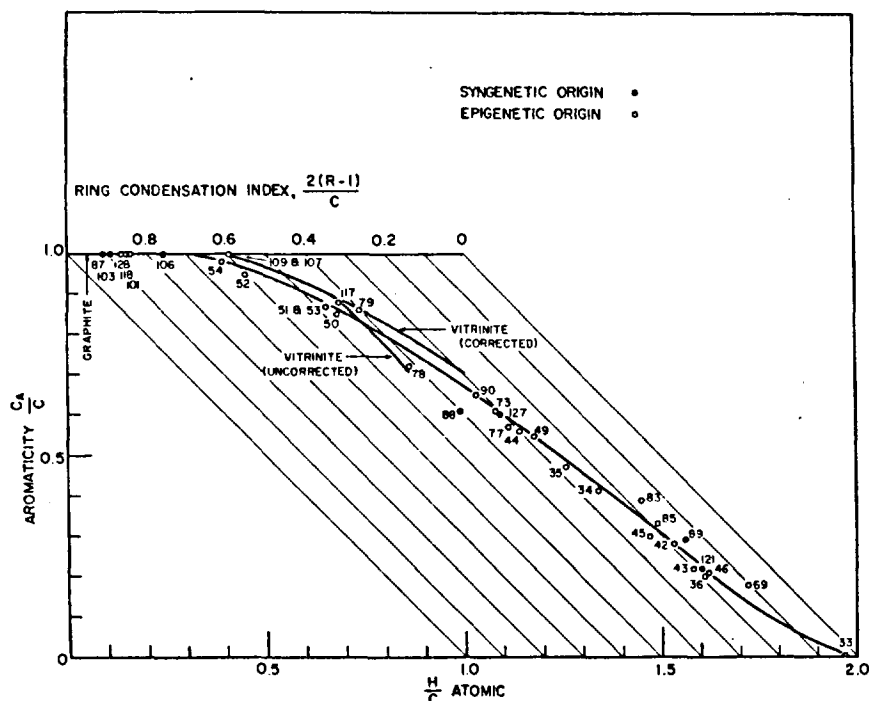


Figure 5 - Relation of aromaticity, atomic H/C, and the ring condensation index for the primary and secondary samples, including vitrinite from coal.

When the experimental data are plotted in terms of the aromaticity and atomic H/C ratio in Figure 5, the ring condensation index associated with each point may be readily estimated. Van Krevelen's data (24)(25) on vitrinites have also been added to Figure 5. The high oxygen content of the low rank vitrinites necessitates a large correction to H/C, and both the corrected and uncorrected data are shown. The slight deviation between the curve for the samples of this report and the corrected vitrinite curve, possibly results from the fact that the H/C values for the former have not been corrected for oxygen. The oxygen content of the samples in the 0.85 to 1 aromaticity range are on the average 2-3 percent higher than the vitrinite in the same range. For lack of better data the slight difference between curves cannot be positively interpreted as a structural difference. The proximity of the curves thus implies that for a given atomic H/C ratio the fraction of aromatic carbon atoms is similar even though the materials are of different origin, but it will be suggested later that the aromatic cluster size of these two classes of material differs considerably for a given value of aromaticity.

The aromaticity in Figure 5 increases quite rapidly with respect to composition in the high H/C section of the diagram as previously illustrated in Figure 4. At an H/C ratio in the range of 1.0, the rate of increase of aromaticity gradually begins to decline until it reaches a value of 1.0 (fully aromatic structure) in the H/C range of 0.4.

In the area of rapid increase in aromaticity, that is, the area defined by an H/C ratio of 1.7-1.0, the curve does not change rapidly with respect to the ring condensation index. An increase in aromaticity along this section of the curve might be accounted for by either an increase in the size of the aromatic ring systems with the degree of compactness remaining constant, or an increase in the number of aromatic ring systems with their average size remaining constant. (See Appendix for further details.) The latter view is more consistent with the refractometric results presented later in this report which suggest that the average aromatic cluster size remains constant and the aromaticity increases by virtue of an increase in the number of clusters.

Naphthenic rings are probably also present over much of the 1.7-1.0 H/C range and are probably quite abundant above 1.5. This is suggested from the discussion in the Appendix, as well as by the data of Table 5.

In the 1.0-0.4 H/C range the ring condensation increases quite rapidly, presumably resulting from an increased degree of ring fusion. Beyond this range, through the semi-graphite to graphite stage, the aromaticity remains equal to 1.0, and the ring condensation index increases rapidly as a result of the formation of fully condensed crystalline structures.

Additional structural interpretation is possible for some of the samples in the high hydrogen portion of the diagram where molecular weights were obtained on samples 42, 45 and 46. Application of the Montgomery-Boyd (20) method of structural analysis to these data provides information on the distribution of aliphatic, naphthenic and aromatic carbon types, as well as an estimate of the number of rings per molecule. The results of this analysis, expressed in terms of paraffinic, naphthenic and aromatic carbons, are shown in Table 5. This table gives some appreciation of the type of balance that can exist between chemical types in the samples of high H/C ratio illustrated in Figure 5.

Refractive Index and Aromatic Cluster Size

The refractive index of organic materials is a function of both aromaticity and aromatic ring fusion. Its development with respect to atom percent carbon is shown in Figure 6. The refractive index increases initially at a relatively constant rate to approximately 45 atom percent carbon beyond which it increases at a declining rate and extrapolates to a value between 2.05 and 2.1 for 100 percent carbon, suggesting a value within this range

TABLE 5

Montgomery-Boyd Structural Analysis of Samples
42, 45 and 46, Reduced to Three Parameters

Sample	Molecular Weight <u>1/</u>	No. of Carbon Atoms per Average Molecule	No. of Carbon Types per Average Molecule			No. of rings per Average Molecule	Ring Condensation Index	Percent Distribution of Carbon Types		
			C _P	C _N	C _A <u>2/</u>			C _P	C _N	C _A
46 Liverite	850	58.7	31.5	14.5	12.7	5.7	0.16	53.6	24.7	21.7
42 Tabbyite	970	68.4	37.5	11.3	19.8	7.1	0.18	54.6	16.5	28.9
45 Gilsonite	1500	107.0	47.2	27.3	32.5	14.5	0.25	44.1	25.5	30.4

1/ Number average molecular weight determined cryoscopically in phenanthrene.

2/ C_P, C_N, C_A - Paraffinic, naphthenic and aromatic carbon types, respectively.

for the maximum index of graphite. McCartney and Ergun (28) obtained values of 2.15 and 2.04 for the maximum and minimum refractive indices of crystalline graphite.

Refractive index data on vitrinite, exinite and micrinite, after van Krevelen (24)(25), are included in Figure 6 for comparison. Differences between the macerals, as well as between the macerals and the samples under consideration, are quite apparent below 60 atom percent carbon. Above 60 atom percent carbon the vitrinite follows the curve described by the data of this report, but the micrinite follows a track of higher refractive index. Exinite has the lowest refractive indices for the macerals over the coalification range covered by the data, but by means of a slight extrapolation the exinite branch appears to cross the main curve and join the micrinite branch. This means that as coal increases in rank the exinite eventually acquires a higher refractive index than its associated vitrinite in the same specimen. This is evident in the Pocahontas coals of low volatile bituminous rank, where in thin section the exinite is more opaque than the surrounding vitrinite, or in reflected light the exinite has a higher reflectance.

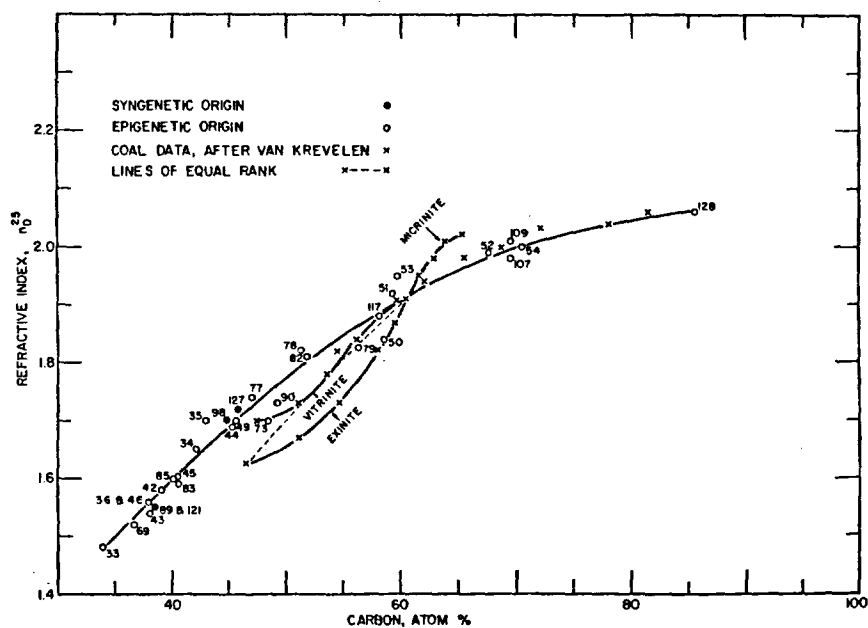


Figure 6 - Relation of refractive index to atom percent carbon for the primary and secondary samples, including the coal macerals.

When the refractive index is plotted with respect to aromaticity (Figure 7), the above-mentioned differences between the coal macerals and the samples of this report continue to persist up to an aromaticity of approximately 0.90, suggesting that for a given level of aromaticity the size of the fused aromatic clusters (the size of the aromatic structural unit) could be different. This structural implication can be further justified by a consideration of the molar refraction with respect to aromaticity and aromatic cluster size. Van Krevelen (29) has shown that the reduced molar refraction satisfies the condition that it is an additive property and at the same time a function of the aromatic cluster size or number of aromatic carbon atoms per fused aromatic structural unit (C_{au}). In other words, the difference between the reduced experimental molar refraction and the sum of the atomic contributions per atom of carbon is equal to the molar refractometric increment (I_M/C), and this structural factor is in turn a function of C_{au} . In order to demonstrate these views Schuyer, Blom and van Krevelen (30) assumed that the π electrons within a fused cluster have a mobility similar to that of the valence electrons in metals, and with the aid of a simple model were able to calculate the polarisability and the molar refraction of a series of polynuclear compounds to an accuracy of ± 2 carbon atoms per cluster.

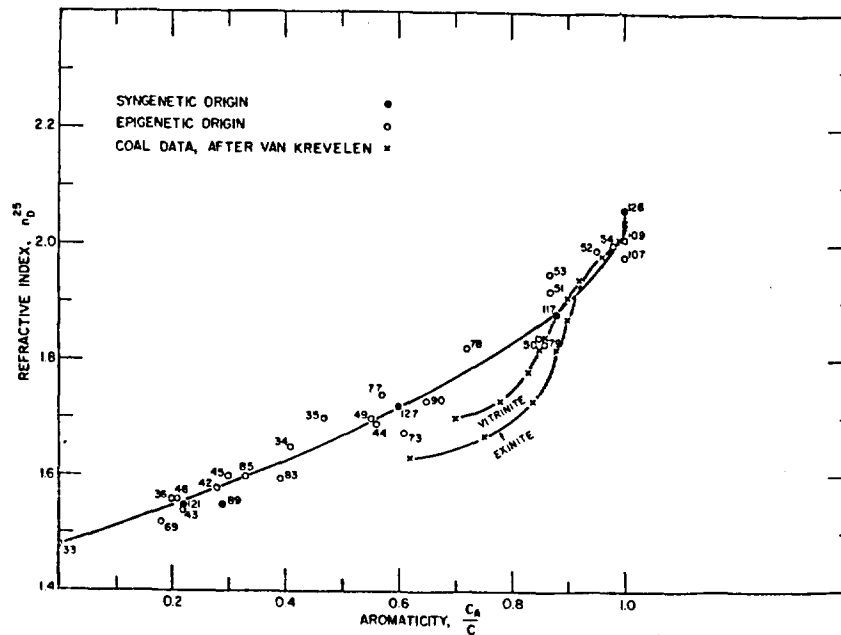


Figure 7 - Relation of refractive index to aromaticity for the primary and secondary samples, including the coal macerals.

In applying the refractometric method to coal, these investigators found that the molar refractometric increment per aromatic carbon atom (I_M/C_a) showed a rather sharp decrease in the medium rank range and they attributed the decrease to a charge transfer between lamellae in the crystallites. This phenomenon imparted an upper limit to the method.

The molar refractometric increment was obtained from the following equation:

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M_c}{d} = 2.558 + 1.039 \frac{H}{C} + 1.65 \frac{O}{C} + 2.48 \frac{N}{C} + 7.64 \frac{S}{C} + \frac{I_M}{C},$$

where

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M_c}{d} = \text{the reduced molar refraction, and}$$

$$I_M/C = \text{the refractometric increment.}$$

The atomic refractions used in the above equation are the same as those used by van Krevelen (1) for coal. The values for the number of aromatic carbon atoms per structural unit (C_{au}) were obtained graphically, using the relationship between I_M/C_a and aromatic surface area (29). Values for the molar refractometric increment and the aromaticity were smoothed with respect to atom percent carbon for the calculation of C_{au} .

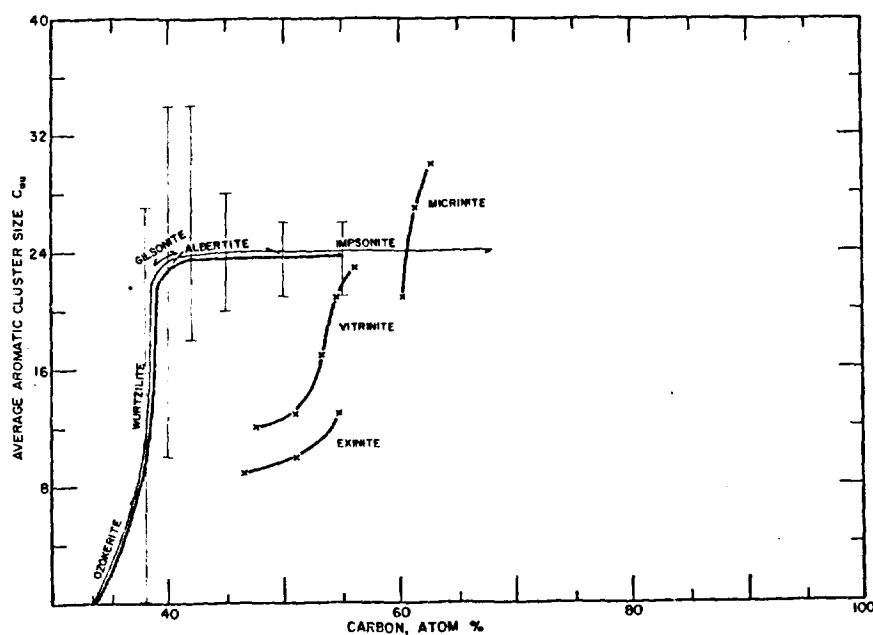


Figure 8 - Line of regression showing the relation of the average aromatic cluster size, C_{au} (the number of aromatic carbon atoms per structural unit), to atom percent carbon for the secondary samples. The only samples of primary origin shown are the coal macerals.

The line of regression for C_{au} with respect to atom percent carbon is shown in Figure 8, as well as the limits of variation. For low carbon values the large variations are in part due to the following conditions: the low concentration of aromatic substance in this class of material; imperfections at the surfaces used for the refractive index measurements; the wide molecular weight range of some of the materials considered, for example, the McMurray asphalt; and the error introduced in evaluating C_{au} . On the other hand, it is probable that at least a portion of the variation is due to actual differences in the average cluster size of the various samples.

Considering the average curve, the aromatic cluster size increases very rapidly and then reaches a relatively constant value of 23-24 C_{au} (5-6 condensed rings) up to the beginning of the range of the impsonites, after which the method is no longer applicable. The data do not preclude the possibility of materials in the wurtzilite range also having values in the 23-24 C_{au} range.

In spite of the uncertainties regarding the application of the refractometric method to materials of such low aromaticity, the results are in good agreement with an X-ray result obtained by Yen, Erdman and Pollack (32) on a gilsonite asphaltene and based on the Diamond method (33). Their value of 9.1 Å for the layer diameter of the aromatic sheets, which is approximately equivalent to 27 C_{au} , is very close to the 23-24 C_{au} value of the refractometric method for the whole gilsonite.

Figure 8, as well as the plot of aromatic cluster size versus aromaticity in Figure 9, clearly shows significant differences in the average size of the aromatic clusters between the low oxygen materials under consideration and the coal macerals, and verifies the structural implications of Figures 6 and 7. In addition to the differences in aromatic cluster size, Figure 9 shows that coal increases in degree of aromatic fusion with increasing aromaticity; whereas, in the gilsonite-impsonite series the average cluster size remains more or less constant with increasing aromaticity. In other words, an increase in aromaticity in the gilsonite-impsonite series involves an increase in the number of aromatic clusters of the same average size. These differences between coal and the secondary materials could convey a specific geochemical implication. It is possible that these differences arise as a result of a process of selection and concentration of preferred molecular and chemical types from the primary sedimented organic matter. The nature of such a process will be discussed later.

It would be desirable to draw a comparison between coal and the high oxygen kerabitumens, such as sample 98, on the basis of this structural parameter for geochemical and classification considerations. Unfortunately, aromaticity data are not available on this sample, so C_{au} could not be calculated.

Volatile Matter and Solubility

The volatile matter of aliphatic and low molecular weight aromatic compounds is high but decreases for high molecular weight polynuclear aromatics. Various workers have attempted to use the volatile matter of coal as a means for determining aromaticity, and van Krevelen (34) has demonstrated that the values are lower than those given by the graphical densimetric method by approximately 10-12 percent for low rank coals, indicating that some aromatic carbon is volatilized. On the other hand, the agreement is close enough to provide a fair indication of coal rank.

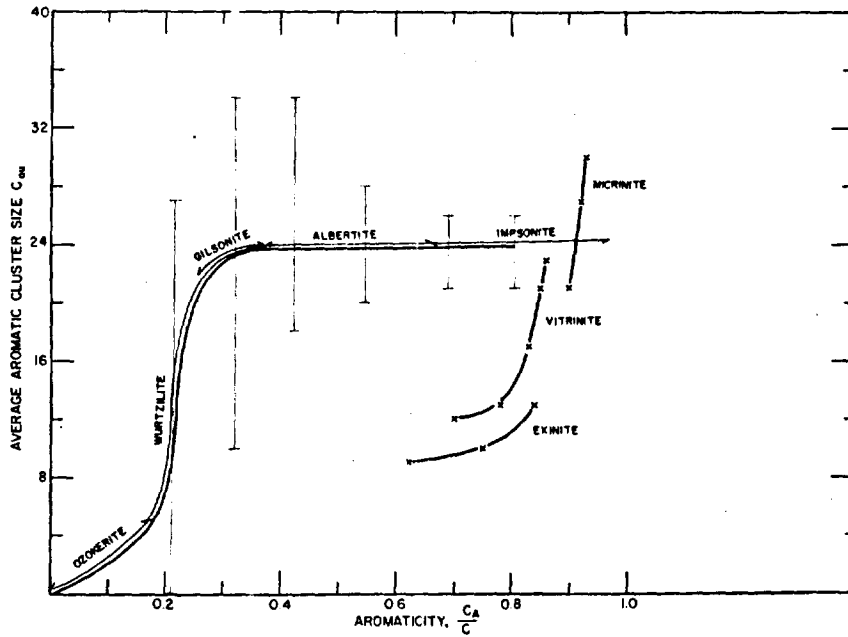


Figure 9 - Line of regression showing the relation of the average aromatic cluster size, C_{au} (the number of aromatic carbon atoms per structural unit), to aromaticity for the secondary samples. The only samples of primary origin shown are the coal macerals.

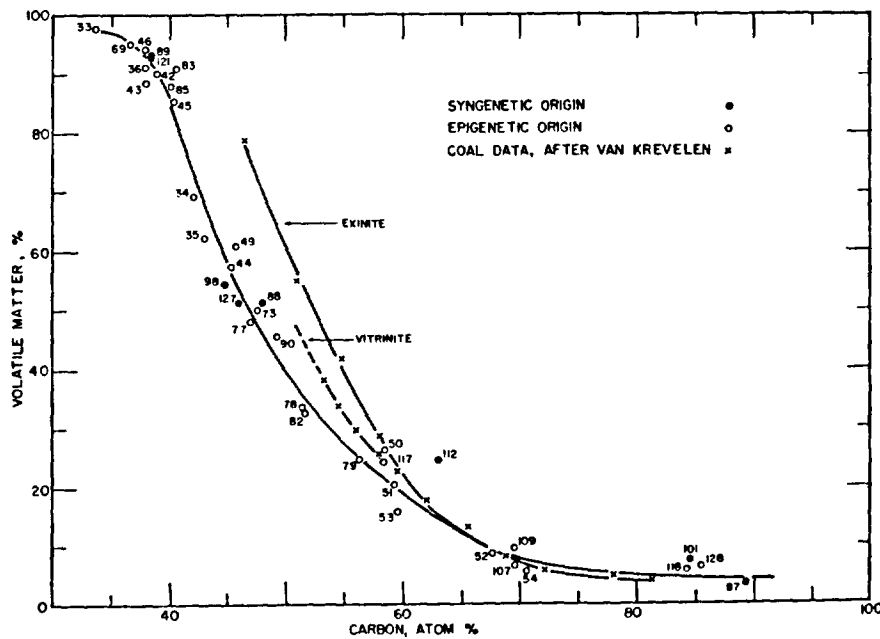


Figure 10 - Relation of volatile matter to atom percent carbon for the primary and secondary samples, including the coal macerals.

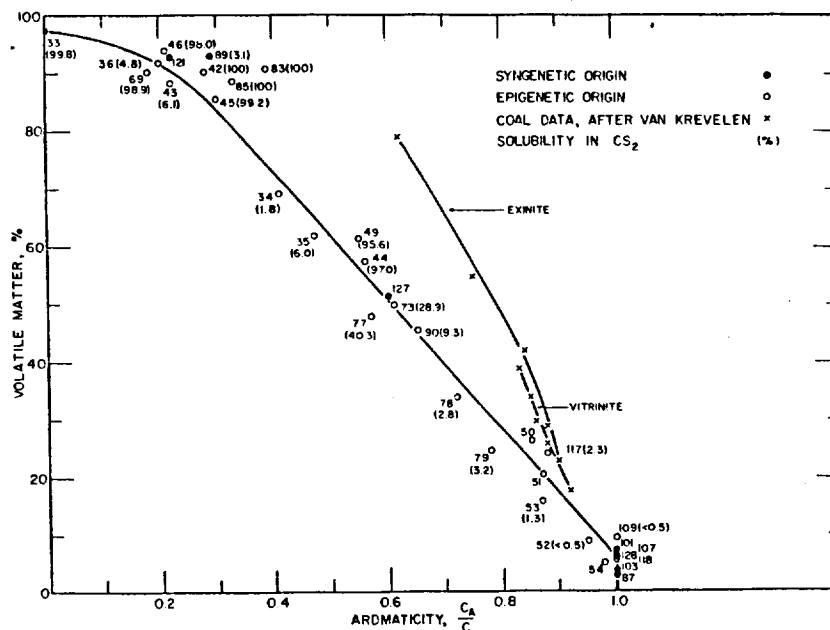


Figure 11 - Relation of volatile matter to aromaticity for the primary and secondary samples, including the coal macerals. Solubility data are also included.

Figures 10 and 11 show that aromaticity is an important structural parameter with respect to volatile matter content for the materials under consideration. In Figure 10 the volatile matter decreases rapidly with increase in atom percent carbon up to approximately 70-75 atom percent carbon, where the aromaticity becomes equal to one. Beyond the 70 percent limit the rate of decrease of volatile matter is slow. The coal maceral data show that for a given carbon content the volatile matter for low rank coal is much higher than that of the samples of this report. At higher ranks the difference becomes small. Figure 11 brings out the variations at the low rank end even more clearly and suggests that the difference in aromatic cluster size indicated by the refractometric data (Figures 6-9) might explain the volatile matter differences. That is, for a given level of aromaticity a larger proportion of carbon atoms is volatilized in coal because of the smaller aromatic cluster size of the coal. This explanation represents the simplest but not necessarily the actual mechanism. The mechanism of pyrolysis and the formation of a coke residue can be extremely complex, as has been shown by the work of Wolfs, van Krevelen and Waterman (35). They have stressed the importance of functional groups in the carbonization of model polymers.

The aromaticity and volatile matter show a straight line relation (Figure 11) through the majority of samples considered, with greatest scatter at the high volatile end. The presence of a low molecular weight fraction is probably responsible for this scatter and is known to exist in samples 83 and 85. Otherwise, the relative molecular weight as indicated by the solubility data does not appear to exert a strong influence on the volatile matter, provided it is higher than approximately 700-900. The limits of scatter are not preferentially determined by either the soluble, partly soluble or insoluble samples, and both the partly soluble and insoluble samples are represented over a wide range of the curve; however, at the high aromatic end the solubility is consistently low.

Structural Information from Infrared Analysis

The characterization of bituminous materials of syngenetic and epigenetic origin from their infrared spectra and the quantitative data derived from these spectra, offer a useful approach to their study, and provide some structural detail not obtainable from other physical properties. Infrared spectra have previously been utilized in studies of some of these substances (2) (3), but principally on the soluble portion, or on fractions separated by other means. Infrared spectra have been used widely in the study of coal (36)(37)(38). Coal spectra have been compared and related qualitatively to absorption bands in pure compounds to elucidate their structure. Brown (36) estimated the ratios of aliphatic hydrogen to aromatic hydrogen from absorption in the 3-micron region.

Relating quantitative data from the pellet spectra of these samples to comparable data from pure compounds provides useful structural information on these types of materials. Earlier studies have been handicapped by the limited number of pure solid hydrocarbons available as references and by the absence of adequate techniques to produce comparable spectral data on insoluble solids.

The spectra of 8 materials of epigenetic origin and 4 of syngenetic origin shown in Figure 12 are representative of the 39 samples studied. These illustrate some of the similarities and differences existing through the broad range of naturally occurring substances. Since these materials are predominantly hydrocarbon in composition, the principal absorption bands are those due to carbon-hydrogen groups. The hydrocarbon groups present absorb at the following wavelengths (in microns) (39)(40)(41):

Aliphatic Groups -

CH ₃	3.38 and 3.48 (CH ₃ attached to an aliphatic carbon)
	3.42 (CH ₃ attached to an aromatic carbon)
	6.85 and 7.27
CH ₂	3.42, 3.50, 6.82 (linear), 6.90 (cyclic), and 13.9 (paraffinic)
CH	3.46 (weak)

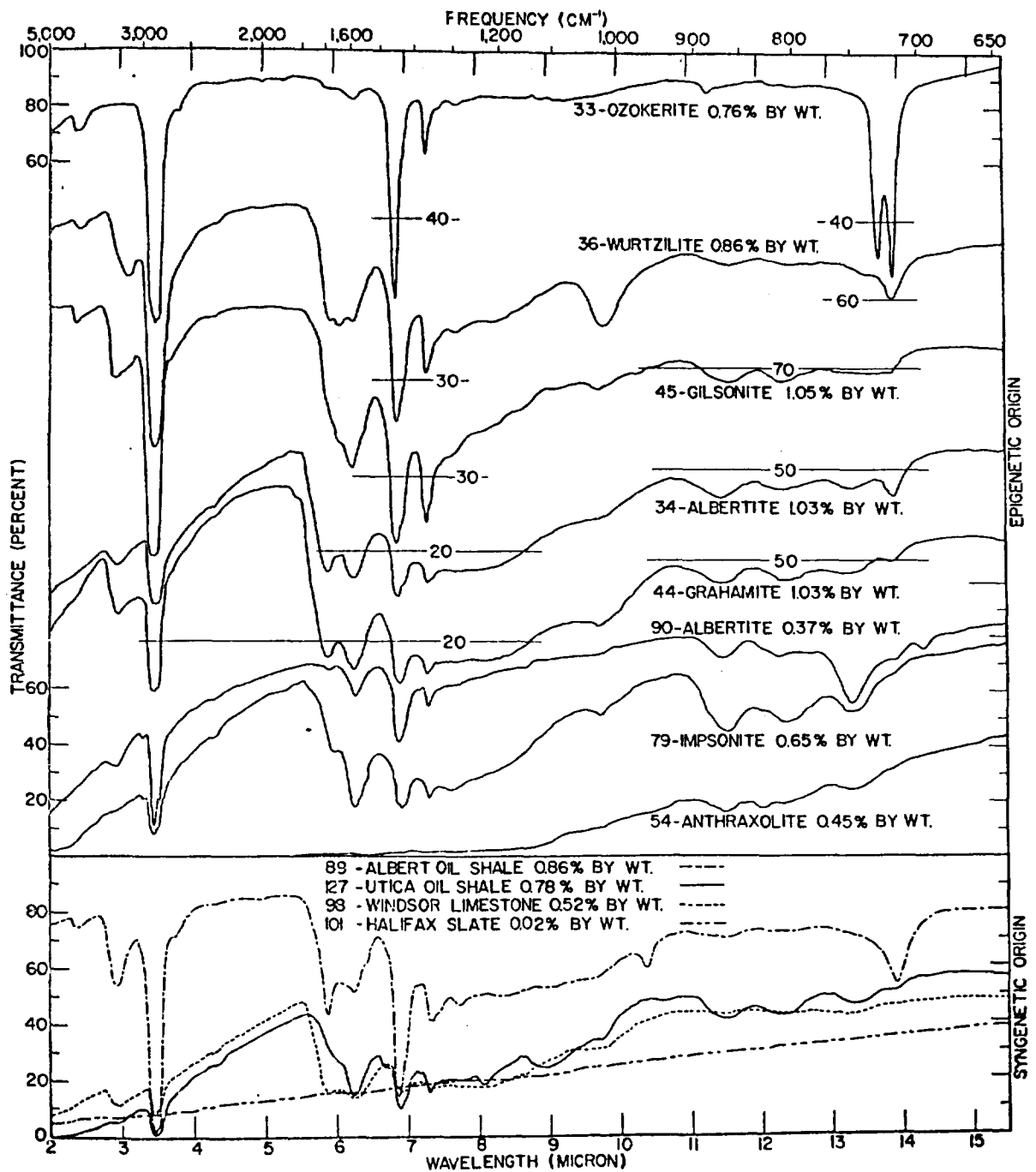


Figure 12 - Infrared spectra of representative primary and secondary samples run in KBr pellets. Designations such as —40— represent percent transmission applicable to the spectrum that the line crosses. The percent transmission scale on the ordinant applies to spectra that are not marked as above.

Aromatic Groups -

CH	3.3	(all aromatic CH)
	11.1 -11.6	(an isolated H on a ring)
	11.6 -12.5	(2 adjacent H on a ring)
	12.35-13.33	(3 adjacent H on a ring)
	13.0 -13.6	(4 adjacent H on a ring)
	13.0 -13.6)	(5 adjacent H on a ring)
	14.1 -14.5)	
C=C	6.25	

In addition to the hydrocarbon groups, absorption bands associated with the oxygen and nitrogen present occur as follows: (in microns)

C=O	5.8-6.0	
C-O-C	7.3-9	(Absorption due to oxygen groups is very broad and not defined in this range.)
OH (bonded)	2.95	(masked by moisture in KBr)
NH	3.0	

A portion of the absorption in the 6.0-6.5 micron region has been assigned to carbon-oxygen linkages (37). Absorption at 9.7-9.9 microns is due to the clay content of the ash.

The spectra, as presented in order of increasing atom percent carbon in Figure 12, illustrate the predominant changes in the proportions of aliphatic and aromatic groups present. The initially dominant aliphatic absorption bands decrease with increase in atom percent carbon. Simultaneously the aromatic absorption bands increase as atom percent carbon increases from 40 to 70. Beyond 80 atom percent carbon, no absorption bands are evident but the general level of absorption is very high. An accurate and significant evaluation of these changes can be achieved only when quantitative comparisons are made. The quantitative data presented in Table 4 and shown in Figure 13 illustrate the type of structural information obtained. The absence of data at specific wavelengths in this table, for some samples, indicates that no suitable or comparable data could be obtained from the spectrum. The structural information calculated for aliphatic and aromatic groups is discussed separately.

(1) Aliphatic Groups

The fractions of the total carbon present in methylene (f_{CH_2}) and methyl (f_{CH_3}) groups were measured from the peak height absorptivities at 3.42 and 7.27 microns, respectively, by comparing the absorptivity of each sample with an average value calculated from the data measured on pure compounds. The average absorptivities derived from the pellet spectra of

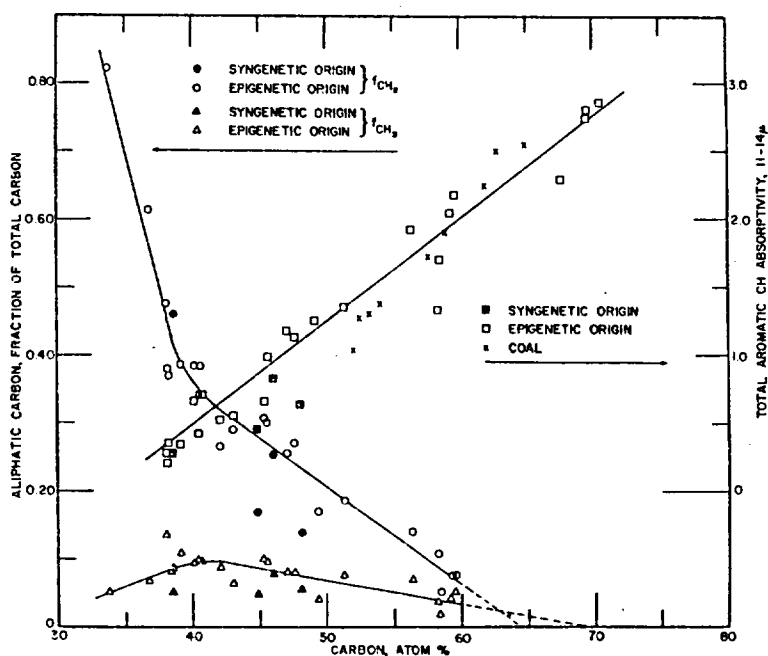


Figure 13 - Relation of quantitative infrared data to atom percent carbon for the primary and secondary materials with some coal data measured in this laboratory.

pure compounds were: 2.80 per gram of methylene at 3.42 microns, and 1.0 per gram of methyl at 7.27 microns.

(a) Methylene Groups - the data on methylene groups include both linear and cyclic types. Some indication of the portion of methylene present in paraffinic chains, $(C_p, (-CH_2-)_n)$, where $n \geq 4$, is given by the absorption at 13.9 microns, and approximate estimates of C_p appear in Table 4. The fraction of the total methylene present in paraffinic chains varies widely throughout the atom percent carbon range and follows a random pattern in the samples studied. No clear distinction may be made between linear and cyclic methylene. Reference to the absorption at 6.8-6.95 microns may indicate whether the absorption of linear groups at 6.82 microns or the absorption of cyclic groups at 6.90 microns is the stronger. The absorption at 6.8-6.95 microns in these spectra appears as a broad band in most spectra, but up to 50 atom percent carbon, or the impsonite group, the stronger absorption is at 6.85 microns (linear) with a shoulder on the 6.95 micron (cyclic) side. However, since the relative intensity of these bands in pure compounds was not established, quantitative information could not be derived. Beyond 50 atom percent carbon, the aromaticity is sufficiently strong to mask significant changes in this region.

The absorption band in the 3.4-3.6 micron region is broader in the natural samples than in the pure hydrocarbons, except for the saturated condensed polycyclic compounds containing a relatively high proportion of CH groups. This type of linkage and the complexity of natural materials could account for this broadening. In some samples a small contribution from bonded OH groups in acid dimers is apparent where carbonyl C=O absorption occurs at 5.8 microns.

In Figure 13 the line following the methylene carbon content, f_{CH_2} , drops sharply from 0.82 for ozokerite at 34.2 atom percent carbon to 0.37 for materials having 40 atom percent carbon. Beyond 40 atom percent carbon the slope decreases to reach a constant value from 45 atom percent carbon on. This trend might extend beyond 60 atom percent carbon, but no samples in this immediate range were available.

The methylene contents of the 2 grahamites are almost identical, and 4 of the 5 albertites are very close despite the differences in atom percent carbon. Two of the four samples of syngenetic origin for which the f_{CH_2} could be measured (samples 89 and 127) are in line with values for the samples of epigenetic origin, but the f_{CH_2} of the remaining two samples (samples 98 and 88) are comparatively low. These low values are of the same order as values calculated from coal spectra currently being measured. Further work may establish reliable trends for different bituminous substances.

(b) Methyl Groups - The methyl carbon content, f_{CH_3} , of the samples varied from 0.02 to 0.14, with the majority of the values falling in the 0.05 to 0.10 range. As shown in Figure 13, the highest values are concentrated in the 38 to 42 atom percent carbon range. The f_{CH_3} is fairly constant within any one class of material; the average values being: 0.10 for the grahamites, 0.07 for the albertites, and 0.05 for the impsontites. As these averages and the values plotted in Figure 13 illustrate, the broad trend established for the secondary materials from 45 to 60 atom percent carbon is for a gradual decrease in f_{CH_3} which could continue beyond 60 atom percent carbon to become zero close to 70 atom percent carbon when the materials become fully aromatic.

The traces of aliphatic groups present in the materials in the 60 to 70 atom percent carbon range would presumably exist as short bridges between aromatic units or as short side chains on these units.

The general trend throughout both the primary and secondary materials is that the aliphatic groups decrease in number with increase in both atom percent carbon and aromaticity. Infrared data give some insight into both the amount and the composition of these aliphatic groups.

(2) Aromatic Groups

As previously shown in Table 3 and Figure 4, the aromatic content increases with increasing atom percent carbon. In the infrared spectra the strongest peaks due to aromatic groups are at 6.25 microns and the sequence of broad bands in the 11 to 14 micron range. The absorption at 6.25 microns is largely due to the aromatic C=C bonds but as mentioned previously this band is partly attributed to oxygen linkages (37). Furthermore, the absorptivity of this band in aromatic compounds is extremely variable and is thus not reliable for quantitative measurements. On the other hand, the absorption in the 11 to 14 micron region does provide useful quantitative information even though the peaks are not well defined.

The bands in the 11-14 micron region, as described earlier, are assigned to varying numbers of adjacent unsubstituted hydrogens on an aromatic ring. In pure compounds the absorption of aromatic CH in this region is very strong; quantitatively stronger than that of any aliphatic CH absorption in the 3-micron region. This absorption, for nearly all samples, consists of very broad ill-defined bands rather than the sharp peaks found in pure compounds. These broad bands are characteristic of the complex nature of naturally occurring organic substances. It was not possible to derive any specific trend using peak height measurements alone, as a large portion of the absorption occurs between the actual maxima. However, using the total absorption in the 11 to 14 micron region (see Figure 1) it was possible to evaluate the aromatic CH content. These absorption values are included in Table 4. As shown in Figure 13, this value increases at a constant rate as atom percent carbon increases from 34 to 70. The correlation of the total absorption with atom percent carbon was calculated by the least squares method for the materials of epigenetic origin. The correlation coefficient of this relationship is 0.98 and the equation for the line of regression is $y=0.075x-2.50$, where x equals atom percent carbon and y equals total absorptivity at 11-14 microns. Although the atom percent hydrogen is decreasing, the absorption due to aromatic CH groups is increasing at a constant rate. These changes are accompanied by a corresponding decrease in the aliphatic CH groups. Beyond 70 atom percent carbon, where the material is essentially aromatic, this absorption must decrease as the hydrogen content continues to decrease. However, no samples in the range immediately beyond 70 atom percent carbon were available and the higher atom percent carbon samples included gave only straight line spectra at the low concentrations necessary to bring the absorption on scale.

Comparable aromatic absorptivity values calculated from 9 coal spectra previously measured in this laboratory are included in Figure 13. These values fall near the line established for materials of epigenetic origin, but when considered independently they follow a line of greater slope than the line for materials of epigenetic origin. Two of the samples of syngenetic origin, 98 and 88, fall well below the line for secondary materials and close to the line of the coal values. In the range of 45 to 55 atom percent

carbon, samples 98 and 88 and the coals contain a higher atom percent oxygen than the secondary materials, which may account for the lower hydrocarbon contents of the whole samples.

To ascertain the relationship of this total aromatic CH absorption with the aromatic portion of the samples under consideration, the absorptivity is plotted against atom percent aromatic carbon. This relationship, illustrated in Figure 14, also appears as another straight line with a correlation coefficient of 0.98 for materials of epigenetic origin. The equation for this line is $y = 0.039x - 0.06$. The aromatic CH increases at a constant rate with increase in aromatic carbon, suggesting that the basic aromatic structure is not changing radically and that the balance of cluster types, or degree of compactness, is remaining relatively stable.

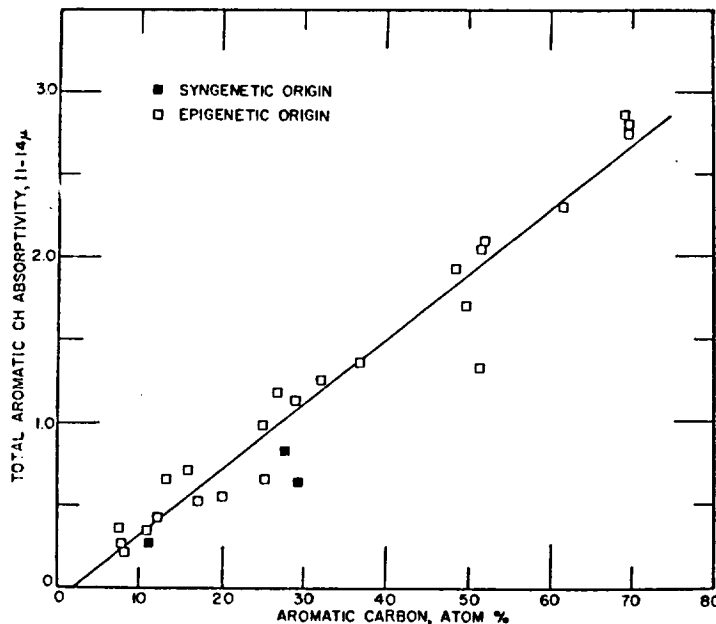


Figure 14 - Correlation of total aromatic CH absorptivity (11-14 microns) with atom percent aromatic carbon.

The relative amounts of each type of unsubstituted hydrogen, that is, an isolated one, and 2, 3, and 4 adjacent hydrogens, may be estimated when the heights and areas of the individual broad bands in the 11 to 14 micron region are compared with pure compounds. For this purpose the average absorptivity peak height values used for pure compounds were:

1 hydrogen	9.5 per gram of carbon
2 hydrogens)	5.5 " " " "
3 ")	
4 hydrogens	4.0 " " " "

A distinction between the 2 and 3 adjacent hydrogen groups is not possible in view of the overlap of the two ranges and the absorption patterns of these samples. Hence the relative values of the 2-3 adjacent hydrogens are not well defined. The number of groups of 4 adjacent hydrogens is generally greater than those of isolated hydrogens or 2-3 hydrogens for materials up to and including 40 atom percent carbon. For the higher atom percent carbon materials, including albertites, grahamites, imponites and anthraxolites, the number of isolated hydrogens exceeds the number of groups of 4 adjacent and the number of groups of 2-3 is intermediate. Albertite sample 90 is the only material with absorption beyond 14 microns, indicating the presence of 5 unsubstituted adjacent hydrogens on a ring. This sample also contains a much higher portion of 4 adjacent hydrogens than any other material.

Included in Table 4 is the total of f_a and f_{CH_2} and f_{CH_3} for 25 samples. These totals should theoretically be less than 1.0 to allow for carbon atoms present in other groups, or equal to 1.0 if no other such groups are present. The total values, in general, appear to fall within these limits and indicate that the methods used to obtain them are fairly reliable. For cases where this total is low and the foreign atom content of the material is not excessive, it may be assumed that these materials contain a relatively high portion of saturated carbon with no hydrogen attached or only one hydrogen attached. From this it may be concluded that samples such as 43, 36, 42, 45 and 34 would contain a larger number of branched chains or saturated cyclic units than the other samples studied.

(3) Background Absorption

In addition to the information gained from absorption bands due to specific structural groups, the background absorption of these materials also provides an infrared spectral characteristic. This characteristic was measured at 5 microns where no absorption due to functional groups occurs, as may be seen qualitatively from the spectra shown in Figure 12. The absorptivities at 5 microns are listed in Table 4, and are shown plotted against atom percent carbon in Figure 15. Comparable data from coal spectra available in this laboratory are included in this figure. This plot indicates the general trend to higher background absorption with higher atom percent carbon for all materials.

For the lower atom percent carbon, highly aliphatic materials, this value is of little significance, as the background is very small; furthermore, strong absorption bands are available for quantitative information on these materials. This absorption is of interest for the higher atom percent carbon materials, especially for those having over 70 atom percent carbon where the background value constitutes the only measurement which can be used to characterize an otherwise featureless spectrum.

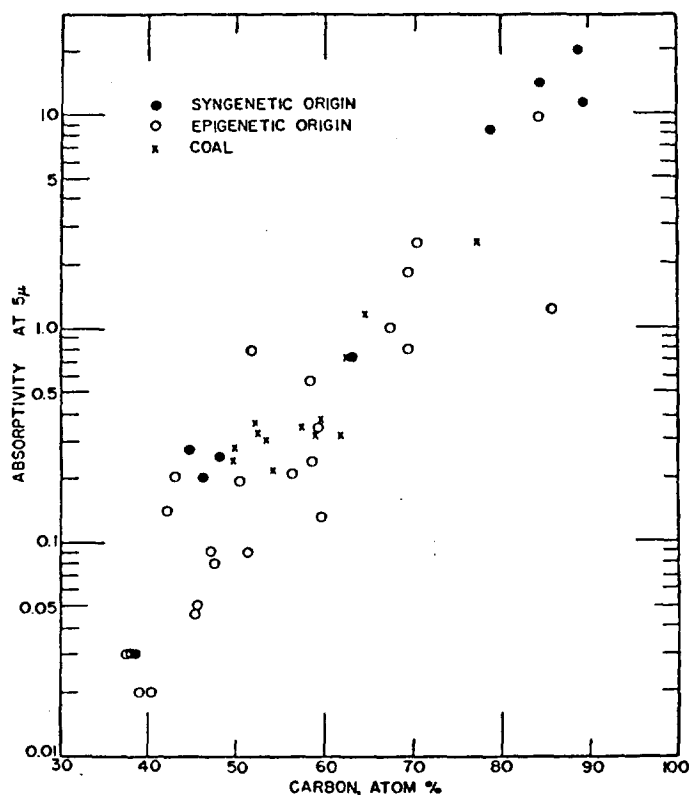


Figure 15 - Relation of background absorption at 5 microns to atom percent carbon.

Particle size measurements made on a number of the higher atom percent carbon samples indicate that particle size is not the principal cause of background absorption. For sample 87 the average particle size was close to 4 microns and the absorptivity 11.2; for impsonite 117 the average particle size was approximately 17 microns and the absorptivity 0.13; and for sample 101 the average particle size was reduced from 40 to 17 microns without altering the level of absorption. These results, and the fact that this absorption increases with carbon content, show that particle size is not the main cause of this absorption.

Another factor considered to influence background levels is the change in refractive index (42), or specifically, the difference between the refractive indices of the sample and the pellet medium. The refractive index of KBr is 1.56. For the samples of known refractive index there is no direct correlation between this difference and the 5 micron absorption. Where the background absorption is greatest, no refractive index values are available.

Brown (36) attributes the development of this strong structureless absorption in the spectra of high carbon coals to the transition of an aromatic structure to a graphite-type lattice. This agrees with the conclusions drawn from other physical properties of the high carbon materials

considered in this report. Graphite itself gives the same high-absorption, structureless spectrum as do the high atom percent carbon materials studied.

GENESIS, STRUCTURE, AND CLASSIFICATION

In matters pertaining to the problem of formulating a classification system for the whole spectrum of organic materials related to geological formations, the purpose for which the system is designed and the premise on which it is based are of fundamental importance. The object of the present discussion is to further the development of a classification system for scientific purposes, and, more specifically, to develop one to best serve the requirements of both the geological and chemical disciplines, since most of the problems concerning organic matter in geological formations are geochemical in nature. This purpose is believed to be essentially the same as that set forth in Resolution 4 of the Third World Petroleum Congress. At that time the Permanent Council appointed a committee to implement the resolution, and two reports have subsequently been published regarding classification (43)(44).

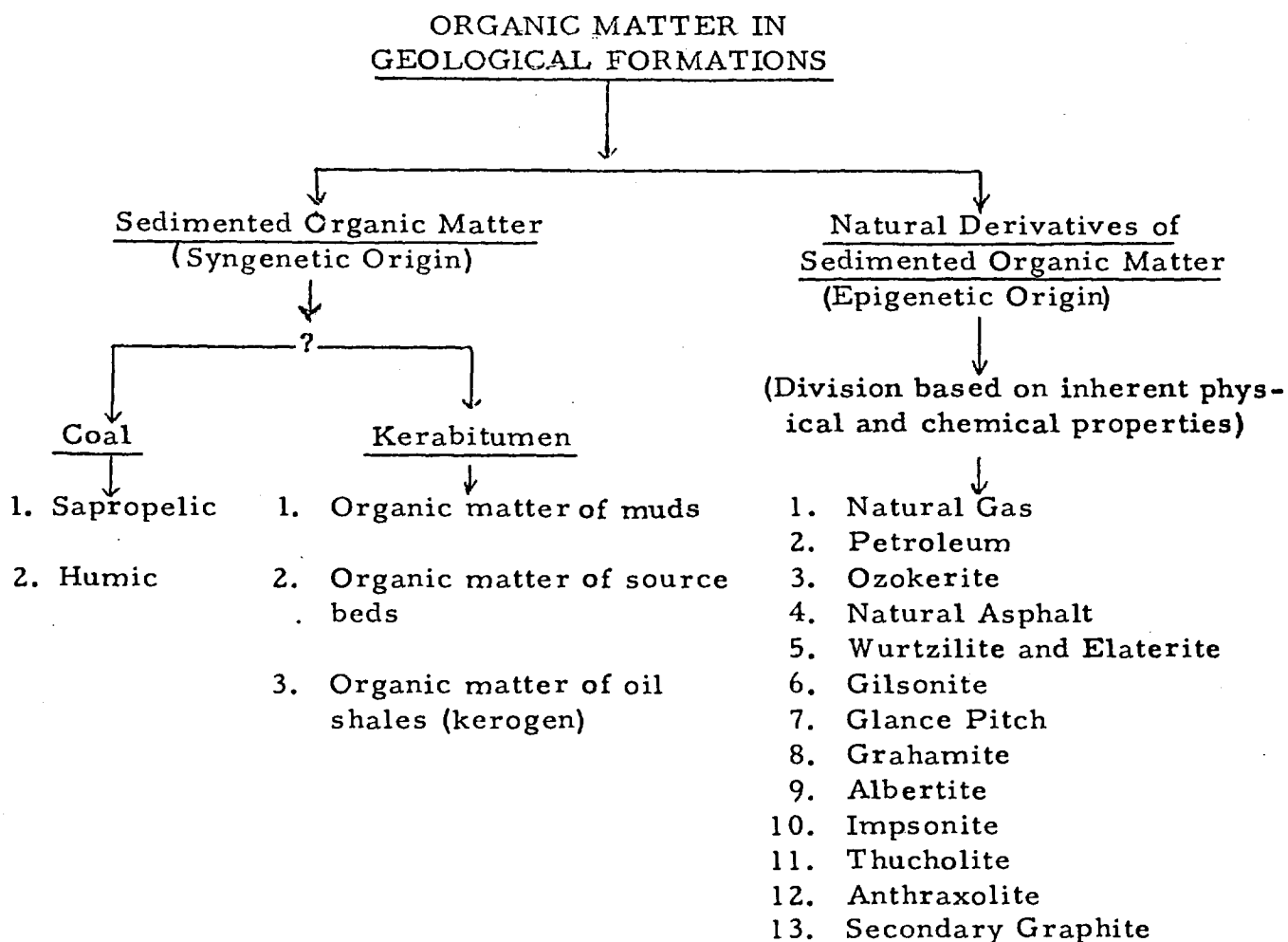
The premise or choice of parameters is a problem of utmost importance and one to which there are many ramifications. This discussion emphasizes the importance of genesis in the classification of organic matter and makes the initial distinction on the basis of a syngenetic or epigenetic origin as indicated in the classification scheme of Table 6. Twenhöfel (45) also divided carbonaceous substances into primary and secondary deposits.

Following the genetic breakdown the natural derivatives of sedimented organic matter can be logically subdivided on the basis of chemical parameters, but the sedimented organic materials require further geological qualification before subdivision based on the inherent chemical properties can be made without creating extensive overlap and ambiguity. On the basis of existing data complete subdivision of this branch would be premature; however, some of the factors related to the problem will be discussed later. To facilitate presentation of the present data, the subdivisions coal and kerabitumen have been used after the most recent classification scheme presented by the World Petroleum Congress Committee (44). This scheme is illustrated in Table 7 and shows the source of some of the nomenclature and ideas incorporated in Table 6. Abraham's classification (1), as well as a scheme adapted from Abraham by Hunt, Stewart and Dickey (2), is shown in Tables 8 and 9.

One of the strongest arguments in favor of the genetic approach is that it greatly reduces the possibility of having materials of a different geological development classified in the same group; a situation common to classifications based entirely on chemical parameters. When materials of a different geological origin are placed in the same group, the classification

TABLE 6

Classification Scheme of Organic Matter in Geological Formations



becomes seriously restricted from the geologist's viewpoint, making it virtually impossible to fit data and conclusions concerning genetic and metamorphic relationships into the classification. Furthermore, oversimplified chemical approaches are not always capable of defining important chemical structural differences between materials within a given group. It is true that the chemical parameters must be as simple as possible for practical reasons, and it is maintained that such a system can only be successful if the materials to be classified are of similar origin and sufficient background material is available to show that the chemical parameter adequately represents a fundamental aspect of the material, even in an empirical manner. A classification that falls short of these considerations defeats its very purpose. Some of the merits and difficulties of a genetic approach have also been discussed by Breger (46). Van Krevelen's enlightened approach to coal is sympathetic to both the

TABLE 7

Classification Scheme of Sedimented Organic Matter and Derived Products
(After Fifth World Petroleum Congress)(36)

<u>Sedimented</u> <u>Organic</u> <u>Matter</u> and <u>Derived</u> <u>Products</u>	<u>Naphthabiten</u> ... (Natural gas of petroleum (Substantially sol- (Crude oil uble in carbon (Natural asphalt disulphide) (Ozokerite (Asphaltite Asphaltoid (Organic matter of muds (vases)
	<u>Kerabiten</u> (Organic matter of source beds (Substantially (Organic matter of oil shales insoluble) (kerogen)
	<u>Coal</u> (Sapropelic coal (Substantially (Humic coal insoluble)

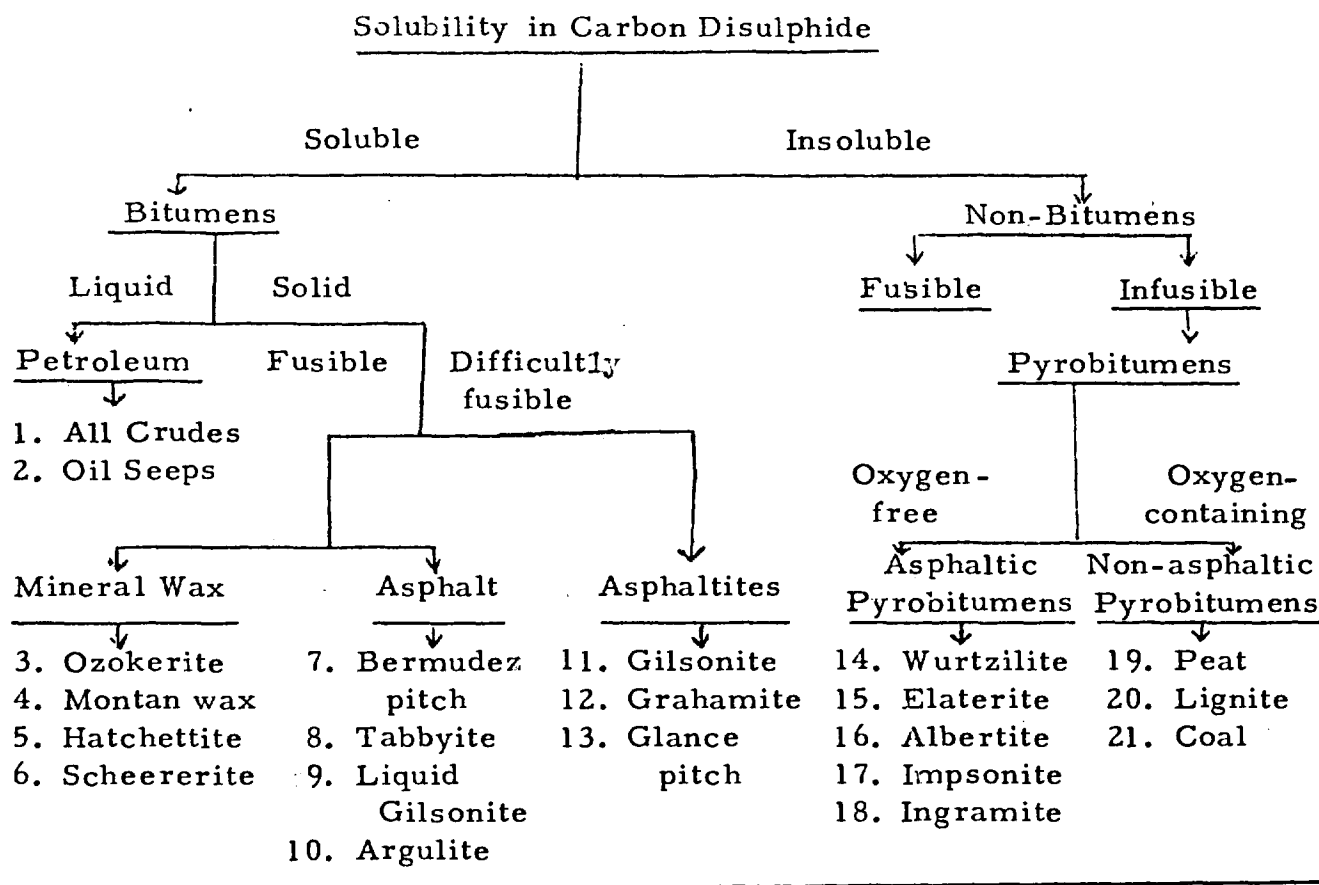
TABLE 8

Classification of Bituminous Substances
(After Abraham)(1)

Genus	Species	Member
Bitumens	Petroleums	Non-asphaltic petroleum Semi-asphaltic petroleum Asphaltic petroleum
	Native mineral waxes	Ozokerite Montan wax
	Native asphalts	Pure or fairly pure Associated with mineral matter
	Asphaltites	Gilsonite Glance pitch Grahamite
Pyrobitumens	Asphaltic pyrobitumens	Elaterite Wurtzilite Albertite Impsonite Asphaltic pyrobituminous shales
	Non-asphaltic pyrobitumens	Peat Lignite Bituminous coal Anthracite coal Lignitic and coal shales

TABLE 9

Terminology and Classification of Naturally Occurring Hydrocarbons
(After Hunt, Stewart and Dickey)(2)



chemical and the geological aspects and strongly indicates that a good classification can be formulated for the entire spectrum of organic matter in geological formations; in other words, a classification through which the geologist can draw broad scientific conclusions.

A basic difficulty inherent in a genetic approach is that an interpretative rather than an objective distinction must sometimes be made, especially when the origin of a material is to be considered in detail; however, for purposes of the present discussion the problem is simplified in that it is only desirable to ascertain a syngenetic or epigenetic origin. The genetic distinction requires a knowledge of the occurrence of the material acquired from the hand-specimen and the field relations. A conclusive decision can generally be made, but in almost any classification uncertainties can be expected to arise. Once sufficient chemical structural data have been accumulated it might also be possible to infer the origin from the chemical information.

Epigenetic deposition is dependent to a large extent on the availability of open space; thus, epigenetic deposits of organic matter generally occur as cavity fillings of various types, for example, fissure veins, and pore-space, breccia and vesicular fillings.

Since the syngenetic organic matter is an original part of the sedimentary rocks its distribution bears a definite relation to the bed, facies, or formation in which it occurs, and a certain compatibility can generally be recognized with the environment of sedimentation. Conditions sometimes arise that provoke considerable argument--in particular, deposits of asphalt impregnated sandstones that are well banded. The banding is suggestive of a primary origin; however, it can often be correlated with lateral porosity variations. A syngenetic origin for such deposits is difficult, if not impossible, to justify in terms of our present knowledge of depositional environments, since reducing environments are generally associated with fine grain deposits formed under conditions of quiescence. Very local occurrences of asphaltic sandstone might possibly be of syngenetic origin, but by far the majority of the large asphalt deposits of the world appear to have formed by virtue of their porosity and their proximity to the margins of large basins and are in fact accumulations of heavy oil (47).

As mentioned previously, the initial genetic breakdown into sedimented organic matter (syngenetic) and natural derivatives of sedimented organic matter (epigenetic) provides sufficient geological qualification for the epigenetic branch, after which the epigenetic branch can be subdivided on the basis of the inherent chemical properties. This leads to a classification of the epigenetic branch compatible with Abraham's classification at the member level, but very different at the species level. For the syngenetic branch, sufficient geological and chemical data are not available on which to base specific improvements, so for immediate purposes the branch is divided into coal and kerabitumen and the chemical data are presented at this level.

Figures 16-18 are ternary diagrams for coal, kerabitumen, and natural derivatives of sedimented organic matter, respectively, on which the elemental analyses are plotted as atom percent carbon, hydrogen and oxygen. For convenience, the atomic H/C and O/C ratios are also indicated. In each diagram the data favour the area close to the carbon-hydrogen axis, showing that the elemental analysis is not definitive with respect to the three major categories.

The diagram for coal (Figure 16) presents a clear picture of the compositional, genetic and metamorphic development of the various macerals of coal. Since normal humic coal is essentially a mechanical mixture of the various macerals, the diagram demonstrates that any comparison drawn between coal and the other natural organic materials should be referred to the maceral basis. The analyses of whole humic coals form a broad band following the development line for vitrain, the major maceral component. The less common sapropelic coals have a more restricted maceral composition and follow the development lines for alginite and exinite.

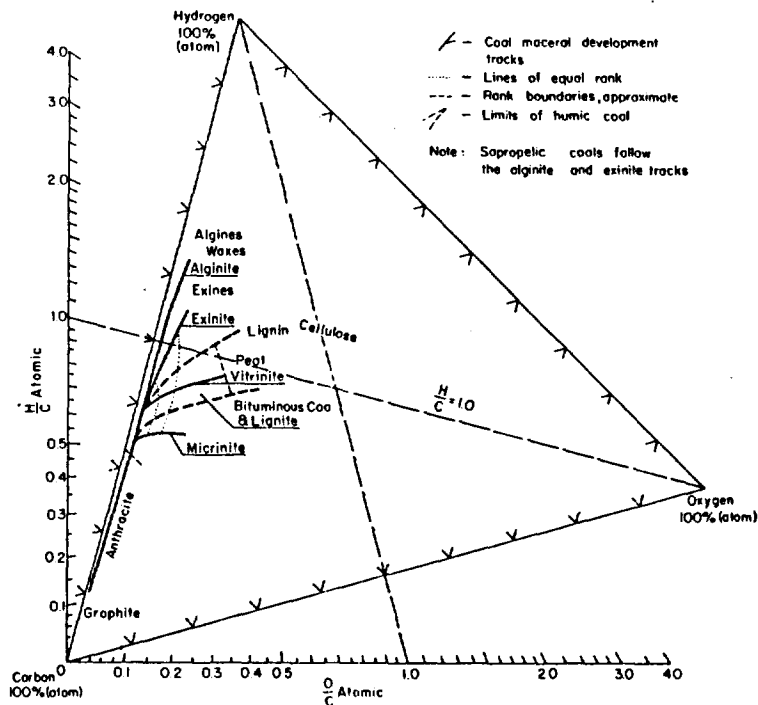


Figure 16 - Coalification of the coal macerals, expressed in terms of atom percent carbon, hydrogen and oxygen, as well as atomic H/C and O/C.

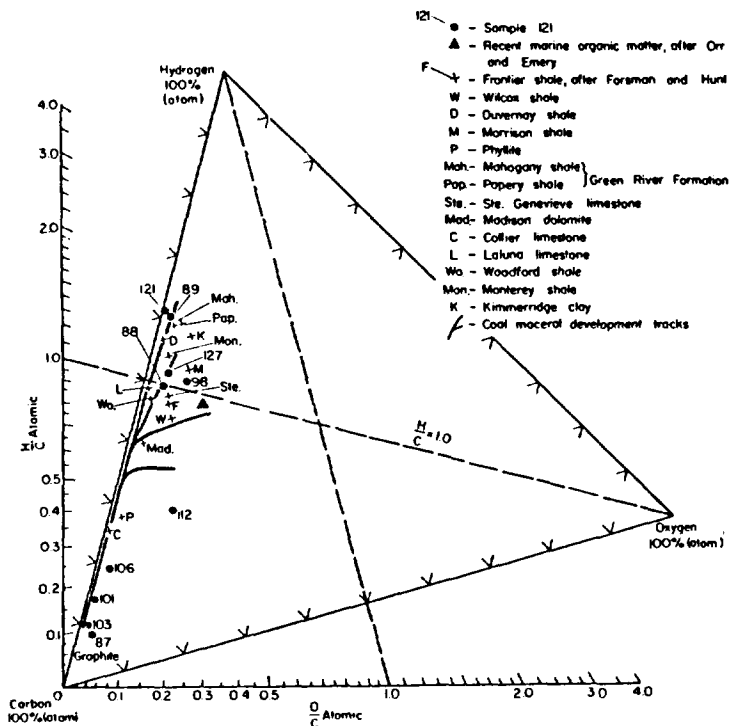


Figure 17 - Kerabitumen samples expressed in terms of atom percent carbon, hydrogen and oxygen. Data are also included after Forsman and Hunt (3), as well as a sample of recent material after Orr and Emery (48). Coal maceral tracks are indicated for comparison.

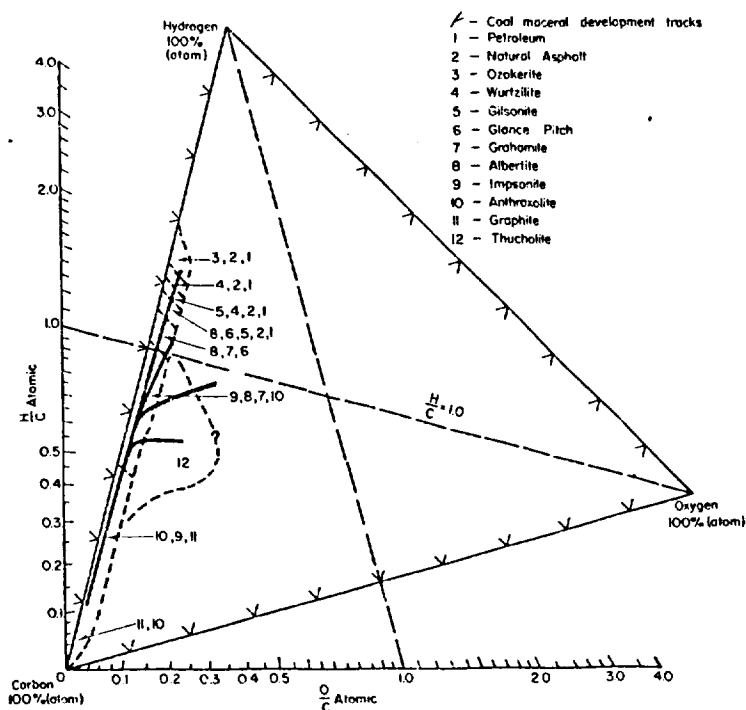


Figure 18 - The natural derivatives of sedimented organic matter (secondary organic matter), expressed in terms of atom percent carbon, hydrogen and oxygen. Coal maceral tracks are included for comparison.

The metamorphic development track of coal is usually referred to as the coalification series, and the degree of coalification is designated as its rank. Rank can, therefore, be used as a "yardstick" for measuring degree of metamorphism. As shown in Figure 16, coal is a mixture of very different macerals each having its respective coalification track or branch. It is important to note that the macerals respond differently to a change in metamorphic conditions, as demonstrated by the lines of equal rank. Each maceral track develops metamorphically in a progressive manner from the original organic sediment (or maceral end member), through continuous stages of increasing aromaticity, and eventually becomes graphite. Such a metamorphic history could be called a "continuous development track".

The kerabitumens of Figure 17 appear to follow a somewhat similar development to that of coal, but for the most part they are devoid of microscopic structure. They commonly occur as minor components in rocks formed under relatively non-restricted environmental conditions, and assume the form of fine grains or films on mineral grains, and some have

oxygen contents similar to low rank humic coals. They are generally present in small quantities in the normal marine environment. When they are deposited under more restricted conditions, their oxygen content is less, they often occur as a major component of the sediment, and they sometimes show well developed morphological structure such as the algae of the typical oil shales. This class of kerabitumen--that is, the typical oil shales--appears to be identical to some of the sapropelic coals both chemically and genetically, and differs only in that it is associated with a high percentage of mineral matter. For purposes of scientific classification the oil shales could well belong to an impure category of sapropelic coal. A similar view is maintained by Schopf (49) and Twenhofel (50). The term 'oil shale' is more easily justified from the technological viewpoint.

Similarly, on the basis of chemical evidence (Figures 16 and 17) no natural break appears to exist between the high oxygen kerabitumens and the humic coals, but there is insufficient knowledge regarding the origin of the former to justify definite conclusions at the present time. Restricting the discussion to marine rocks where the bulk of the kerabitumen substance is found as a minor constituent of the sediment, geologists generally agree that the organic matter is derived from a wide variety of marine plants and animals which might be expected to result in organic accumulations having a sapropelic aspect with higher hydrogen and lower oxygen contents than humic coals. The data of Figure 12 show that kerabitumen can contain relatively large amounts of oxygen, so the possibility arises that the organic sediments undergo considerable oxidative degradation at the time of deposition, resulting in the accumulation of products that on the basis of their elemental analysis resemble humic materials.

An alternate explanation is that humic matter is introduced from terrestrial sources. Breger (5)(6) has noted variations in the hydrogen content of the Pierre and Chattanooga shales, and has attributed them to variable organic contributions from terrestrial (humic matter) and aquatic (sapropelic matter) sources.

Resolution of these contrasting opinions, as presented by Breger and the present authors, has a direct bearing on the classification of sedimented organic matter. For the present time it appears that kerabitumen can best be classified chemically according to its atom percent carbon and oxygen or its atomic H/C and O/C ratios, but only limited genetic and chemical structural conclusions can be drawn from such a classification.

Since the kerabitumens show an overall chemical similarity to coals, they might respond similarly to metamorphic change, but only distribution studies of given beds over varied metamorphic environments can offer direct proof. As a first approximation it might be reasonable to assume that a given kerabitumen of high oxygen content would respond to metamorphic change, at relatively low temperatures, in a manner analogous to the coal maceral track of closest composition; however, possibilities for additional

modification through hydrothermal alteration arise at higher temperatures that might cause a deflection in the kerabitumen track with respect to coal. Neglecting minor deviations in the direction in which the development of kerabitumens might follow as compared to coal, they both proceed to graphite, and it is highly probable that they both progress along "continuous development tracks".

The natural derivatives of sedimented organic matter can be classified in terms of atom percent carbon, volatile matter, and solubility in a logical manner with respect to their aromatic skeletons and, to some extent, their molecular weight. Furthermore, the classification utilizes much of the well known nomenclature of Abraham's classification without serious modification to the latter. The terms anthraxolite and thucholite were not used by Abraham.

Certain chemical aspects of this class of organic material are apparent in the atom percent composition diagram (Figure 18) and are pertinent to the classification. The boundary limits were obtained from Figure 19. With the exception of the thucholites, the secondary organic matter contains less than 4-5 atom percent oxygen, but is spread along the carbon-hydrogen axis to the same extent as the coal and kerabitumen. However, this series does not represent a continuous metamorphic track that develops progressively from sedimentary end members to graphite, as is the case with primary sedimented organic matter. Geological evidence (51)(52) shows that in addition to the operation of the metamorphic variables (temperature, pressure, and time), fractionation, arising from what appears to result from aqueous extraction, becomes an important factor in the development of the secondary series. The evidence suggests the following sequence of events: aqueous extraction of a small fraction of primary organic matter; migration of the soluble fraction to a suitable trap; and deposition of the fraction by means of a suitable release mechanism. In some respects this postulation resembles Baker's (53) solution hypothesis for the origin and migration of petroleum. The resultant deposit is of secondary origin and its chemical composition differs from that of the primary material. The fractionation step imparts a discontinuity to the normal, progressive, metamorphic sequence of events so that the development track representing secondary organic matter might be designated as a "discontinuous development track". The geological evidence also indicates that such a fractionation step can occur at indiscriminate points between ozokerite and the high hydrogen end of the anthraxolites, and the compositional points of departure from the primary track and reentry on the secondary track would depend on the prevailing metamorphic conditions as well as on the actual solution mechanism involved. Once the secondary material enters a track it apparently advances metamorphically in the direction of higher aromaticity in a similar manner to the primary material. It is also suggested that the extraction process is one of selection and concentration of preferred molecular and chemical types from the sedimented organic matter, and that it gives rise in the secondary material to the similar average sizes of aromatic ring clusters previously indicated in Figures 8 and 9.

Thucholite assumes a unique position with respect to the other secondary members because of its association with thorium and uranium, as well as its high oxygen content; however, elemental analysis data are too sparse for the accurate delineation of its boundaries in Figure 18. Hoekstra and Fuchs (21) have noted the unusually high oxygen content of thucholite and suggest that the oxidation occurs as a result of radiation decomposition products of water and, to some extent, by subsequent reaction with hexavalent uranium. They maintain that the aqueous solutions carrying the organic matter as an oil-in-water emulsion locally possess oxidizing powers as a result of the passage of a radioactive particle, and that this results in the oxidation and solidification of the oil, together with simultaneous condensation by radiation. The mechanism for oxidation is most interesting, but it is suggested that radiation need not be invoked to explain the degree of condensation found in the thucholites. The origin of its condensed skeleton is probably similar to that suggested for the adjacent low-oxygen members of the series.

The degree of overlap between subdivisions in Figure 18 clearly demonstrates the need for additional parameters, even though the elemental analysis on the atom percent basis is highly definitive in comparison with the elemental composition expressed on the weight percent basis.

When the subdivisions are defined in terms of atom percent carbon, volatile matter, and solubility they assume a pattern which has been suggested in a previous section, with the aid of Figures 8-11, to depend on the size and distribution of the aromatic clusters. The classification is illustrated graphically on this basis in Figure 19, based on the data of Figure 10.

This classification provides the opportunity of readily detecting basic chemical differences and similarities which are not easily discernible in either the Abraham or the World Petroleum Congress schemes (Tables 7 and 8), since their initial division is on a solubility basis which separates materials that are both chemically and genetically very closely related. For example, the Abraham classification groups together wurtzilite, albertite and impsonite as asphaltic pyrobitumens on the basis of solubility, but Figure 19 shows that these materials cover a very wide compositional range. A similar situation arises with the asphaltites: gilsonite, glance pitch and grahamite; the important fact that grahamite and albertite are chemically similar over much of their range becomes very obscure on the Abraham system, even though they only differ only in solubility, which is an expression of a molecular weight difference. The solubility or molecular weight distinction is important, but it is doubtful whether solubility should take precedence over composition and origin.

Figure 19 also shows that the subdivisions are of unequal scope and some should possibly be subdivided further, for example the impsonites and anthraxolites. Semi-graphite is a term sometimes used for materials approaching graphite and could be recognized here. The range of thucholite is unknown.

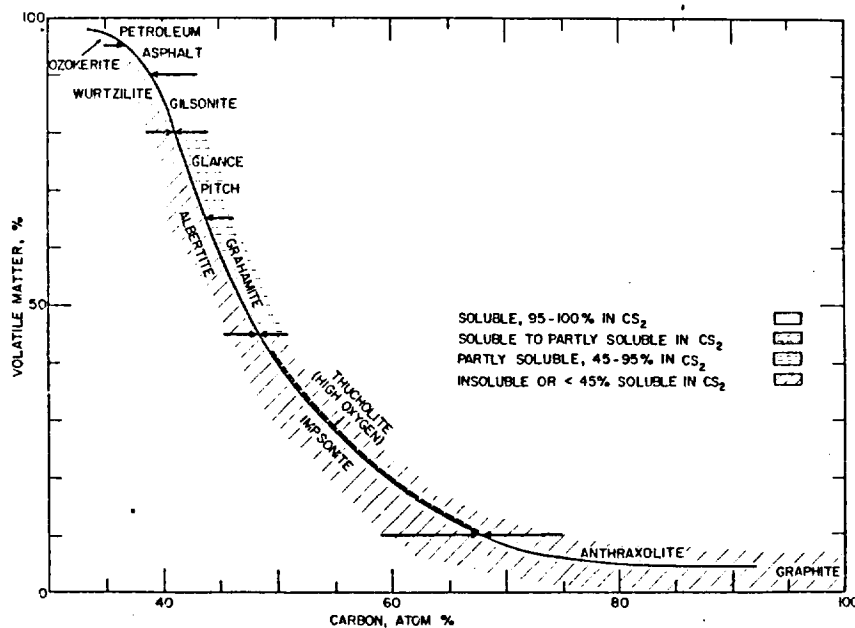


Figure 19 - Classification for the natural derivatives of sedimented organic matter (materials of secondary origin), in terms of volatile matter, atom percent carbon, and solubility.

Abraham (54) differentiated the different asphaltites and asphaltic pyrobitumens with various properties among which the fixed carbon or volatile matter was common to both groups. The classification of Figure 19 utilizes these volatile matter boundaries established by Abraham, with slight modification to those of albertite, wurtzilite and impsonite in order to make albertite correspond more closely with its lower molecular weight counterparts: glance pitch and grahamite. The volatile matter range of albertite was changed from 50-75 to 45-80 and this changed the respective boundaries of wurtzilite and impsonite by 5 percent. Abraham also considered the solubility of grahamite in carbon disulphide to be greater than 45 percent, and this distinction has been followed. Other solubility limits have been designated on Figure 19, but some of the boundaries are probably not as well defined as the manner of presentation suggests.

A certain degree of overlapping between boundaries in Figure 19 can be anticipated, judging from the scatter of points about the curve of Figure 10 from which Figure 19 was derived. To eliminate indecision in such instances, priority should be given either to the volatile matter or to the atom percent carbon, depending on which parameter is more sensitive for the area of the curve being considered. Finally, the influence of solu-

bility on the classification is considered, in order to distinguish between chemically similar categories that differ in molecular weight. For example, the point for an unclassified sample might fall on or near the curve between 45 and 65 percent volatile matter, in which case it would be either a grahamite or an albertite. The third parameter, solubility, would then be used to make the final distinction.

For the extreme high volatile members of the classification the parameters are not definitive, especially for the liquid and semi-liquid members: petroleum and asphalt. Further criteria are required for their classification, such as their rheological properties and various constitutional analysis schemes. The n-d-m method of structural analysis is widely used for petroleum. The sectile properties of wurtzilite, elastic properties of elaterite, and waxy to greasy nature of the ozokerites, are useful diagnostic features of the solids.

SUMMARY AND CONCLUSIONS

Sedimented organic matter and its natural derivatives encompass the entire spectrum of organic matter in geological formations. Owing to large gaps in our knowledge of certain areas of this spectrum, a comprehensive classification suitable to both the geological and chemical disciplines has never been formulated. This study constitutes an attempt to treat, in terms of structural chemistry and geological origin, property data obtained from a wide variety of samples and thereby to further the development of such a much needed scientific classification.

The preparation techniques used in this study to isolate organic matter, of low ash content, suitable for the measurement of reliable physical and chemical properties, are:

- (I) Heavy liquid separation, using a zinc bromide medium. The method is restricted to samples containing pure organic particles larger than 400 mesh, since the fine particles must be removed to prevent flocculation.
- (II) Air-water flotation, for preparing organic isolates from metamorphic rocks. Since the organic matter possesses an internal surface, the application of a slight vacuum to a suspension of the ground rock in water causes bubble formation at the surface of the organic particles. The bubble formation, together with the hydrophobic character of the organic particles, produces a good concentrate at the surface of the suspension.
- (III) Hydrofluoric acid-ultrasonic-settling technique. Carbonates, silicates and silica are removed by hydrochloric and hydro-

fluoric acid treatments. This is followed by an ultrasonic agitation to disperse the insoluble fluorides in the presence of a detergent, and the organic matter is then allowed to settle out; if required, a second differential settling procedure is used to separate organic matter from pyrite. This method can be used for almost any separation problem, provided the organic matter is not seriously altered by the hydrofluoric acid.

For most lithologic types, a combination of at least two of the above techniques is required in order to produce a sample of low ash content. On the average, ash contents can be reduced to approximately 4 percent, but values of less than 1 percent are sometimes obtained.

The property data obtained on the samples have been treated, where possible, according to chemical structural methods developed by van Krevelen for coal. These methods entail the use of the elemental analysis, refractive index, and density. Other properties measured are: infrared spectra, volatile matter content, and solubility in carbon disulphide.

Quantitative structural group data were obtained principally from the infrared spectra of solid materials mounted in KBr, but the nature of a few of the samples necessitated the use of films and solutions. The quantitative data are reported as peak height absorptivities in grams per litre for a 1.0-centimetre thickness. By relating peak height absorptivity data from the KBr pellet spectra of the samples with comparable data from pure compounds ^{1/}, it was possible to determine the fraction of the total carbon present in a specific structural group.

Structural parameters obtained, other than the infrared structural group data, are: aromaticity, reduced molar volume, ring condensation index, and an estimate of average aromatic cluster size. The correlation of these parameters, as well as the measured properties, with atom percent carbon delineates structural trends and development tracks for the materials under consideration. These results are compared with the structural and metamorphic trends in coal. The elemental analysis expressed on an atom percent basis is also useful for classification purposes.

The relation of density to atom percent carbon (Figure 2) shows the development tracks for the materials under consideration as compared with coal. Although the curve depicts major structural reorganizations, only a qualitative structural assessment can be made. The experimental molar volume per carbon atom related to atom percent carbon (Figure 3) indicates, in addition to major structural reorganizations, that the oxygen groups are, on the average, of such a type as to have made a similar atomic contribution

^{1/} The methods of determining and relating these data will be published in greater detail in a subsequent report by one of the authors (FEG).

to the molar volume as did hydrogen at the same atom percent carbon values. Samples containing oxygen groups differing in type from those of the neighbouring samples show an abnormal shrinkage, indicated by a departure from the curve.

The relation of aromaticity to atom percent carbon shows that the former increases with atom percent carbon, and becomes equal to 1.0 (fully aromatic structure) in the 70 to 75 atom percent carbon region. A more fundamental plot, relating the aromaticity, the ring condensation index and the H/C ratio, is shown in Figure 5. In the area of rapid increase in aromaticity, that is, in the area defined by an H/C ratio of 1.7 to 1.0, the curve does not change rapidly with respect to the ring condensation index. An increase in aromaticity along this section of the curve can be interpreted as an increase in the number of aromatic ring systems, with their average size remaining constant; although other interpretations are equally possible, this interpretation is more consistent with the refractometric data. Naphthenic rings are also present over much of this range. In the 1.0 to 0.4 H/C range the ring condensation index increases quite rapidly, presumably as a result of an increased degree of ring fusion. Beyond this range the aromaticity remains equal to 1.0, and the ring condensation index increases rapidly as a result of the formation of fully condensed crystalline structures.

Since the refractive index of organic materials is a function of both aromaticity and aromatic ring fusion, the plot of aromaticity against refractive index (Figure 7) suggests that many of the samples under consideration have a different average aromatic cluster size than coal. When average aromatic cluster size, obtained from the refractometric analysis is related to atom percent carbon and to aromaticity (Figures 8 and 9 respectively), it is clearly shown that the samples of secondary origin have a larger average aromatic cluster size than coal, for a given level of atom percent carbon or aromaticity. Figure 9 also shows, however, that whereas coal increases in degree of aromatic fusion with increasing aromaticity, an increase in aromaticity for material of secondary origin involves an increase in the number of aromatic clusters of the same average size. No data are available on the samples of primary origin, other than those for coal.

Differences between coal and the samples of secondary origin are also apparent in Figures 10 and 11, in which the volatile matter is related to atom percent carbon and aromaticity. The higher volatile content of the coal, for a given level of aromaticity, suggests that a larger proportion of carbon atoms is volatilized in coal because of the smaller aromatic cluster size of the coal.

The quantitative data derived from the infrared spectra help verify the structural picture of the carbon skeleton obtained from the other properties, and provide additional structural detail unobtainable from them.

The spectra of Figure 12 illustrate the predominant changes in the proportions of aliphatic and aromatic groups present. The initially dominant aliphatic absorption bands decrease with increase in atom percent carbon. Simultaneously, the aromatic absorption bands increase as atom percent carbon increases from 40 to 70. The trends of the methyl and methylene groups with respect to atom percent carbon are shown in Figure 13. Also illustrated is the straight-line relation of total aromatic CH absorptivity (11-14 micron region) with atom percent carbon; this relation suggests that the basic aromatic structure is not changing radically, and that the balance of cluster types, or degree of compactness, is remaining relatively stable. Beyond 80 atom percent carbon, no absorption bands are present, but the background absorption, which can also be measured quantitatively, is high.

For purposes of classification, organic matter in geological formations is divided into two major groups on the basis of origin: sedimented organic matter (syngenetic); and natural derivatives of sedimented organic matter (epigenetic). This study shows that the epigenetic material can be effectively classified in terms of atom percent carbon, volatile matter content, and solubility. On the other hand, it appears that a further subdivision of the material of the syngenetic group is required before this material can be classified in terms of simple inherent chemical properties. More complete data on the occurrence, origin and constitution of these materials would be required before such subdivision could be safely established.

With regard to the development of the syngenetic and epigenetic materials, this study suggests that the syngenetic or primary organic matter develops in response to metamorphic influence, in the direction of increasing carbon and aromaticity. The course of the development tracks for the epigenetic or secondary material is influenced by fractionation, in addition to the metamorphic control, and it is suggested that compositional changes arise from processes of selection and concentration of organic fractions from the primary organic matter. It is further contended that the organic fractions migrate in an aqueous environment and can be deposited at indiscriminating stages of development along the secondary tracks.

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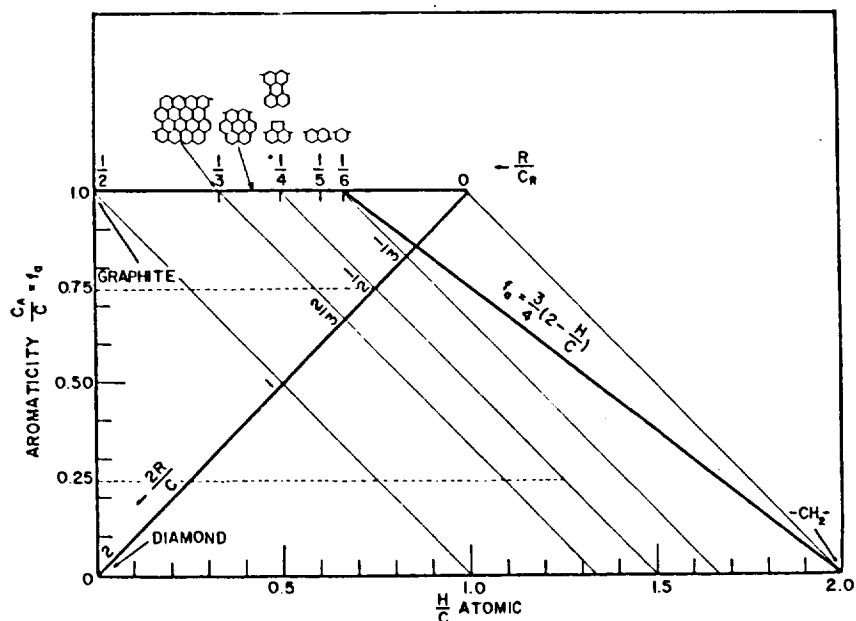
APPENDIX

Theoretical Aspects of the f_a versus H/C Diagram, Applied to the Elucidation of the Structure of Naturally Occurring Organic Materials

by

M. F. Millson*

In the study of coal, bitumen and similar complex substances which are essentially hydrocarbons, much use is made of the quantities f_a (the fraction of the carbon atoms which are aromatic) and H/C (the atomic hydrogen to carbon ratio). In hydrocarbon molecules these quantities are related by the expression $f_a = 2 - H/C - 2(R-1)/C$, where R is the number of rings per molecule; the term $2(R-1)/C$ has been called the ring condensation index by van Krevelen. The following observations upon this and similar relationships were made as a result of discussion of the properties of samples described in the main section of this report.



(1) Numerous loci may be drawn in the f_a versus H/C diagram, to form a background against which the composition of naturally occurring substances may be viewed. For instance, the straight line joining the points (1, 1) and (2, 0) is the locus of the points representing the molecules that would be obtained on progressively lengthening one or more aliphatic side chains attached to a single aromatic ring. In the limit, as the side chain is extended the H/C ratio approaches 2 and f_a approaches zero.

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(2) Consider the series of hydrocarbon structural units of the general formula $\left[C_x H_{2x} - (O)_y \right]$: of all possible repetitive totally aromatic structural groups the single ring has the highest H/C ratio, and of all non-aromatic repetitive groups those of the greatest H/C value are aliphatic with an H/C ratio of 2. Therefore, at any particular level of f_a the hydrocarbon structural unit of greatest H/C ratio will conform to the general formula above. It follows that in the f_a versus H/C diagram the locus of all points representing units of the type $\left[C_x H_{2x} - (O)_y \right]$ as f_a varies from zero to unity will constitute a limit in the direction of increasing H/C for all repetitive hydrocarbon structural units and for infinite polymers formed from them. (Real substances might exceed this limit, but only by an amount not greater than that corresponding to two hydrogen atoms per molecule.)

In any structural unit of the form $-C_m H_n -$ (or in a macromolecule $H - C_a H_b - H$ of sufficient size that the terminal hydrogen atoms may be neglected),

$$H = 2C - C_A - 2R,$$

$$\text{or } C_A = 2C - H - 2R,$$

$$\text{and } f_a = 2 - H/C - 2R/C;$$

where C and H are the numbers of carbon and hydrogen atoms, R the number of rings, C_A the number of aromatic carbon atoms, and f_a the fraction of the carbon atoms which are aromatic.

For structures of the general formula $\left[C_x H_{2x} - (O)_y \right]$ we have:

$$R = \frac{C_A}{6} = \frac{C}{6} f_a.$$

Substituting this value for R in the general expression for f_a , we obtain:

$$f_a = 2 - H/C - f_a/3$$

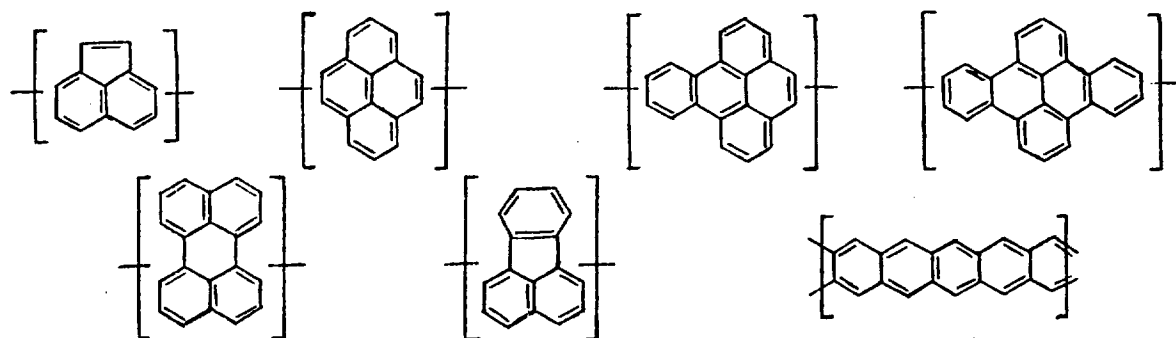
$$\text{or } f_a = \frac{3}{4} (2 - H/C),$$

which is the equation of the locus of points representing structures of the general formula above.

It is evident that this locus is a straight line and that the ends of the locus (2, 0) and (0.66, 1) represent the extreme variations of chemical type, polymethylene and polyphenylene. In general, infinite polymers containing only aromatic and aliphatic groups are represented by a series of loci joining the point (2, 0) with points on the $f_a = 1$ boundary corresponding to the aromatic ring cluster, or average cluster, in the particular repetitive unit.

(3) Saturated polymers, and other molecules where the contribution of two terminal hydrogen atoms to the total hydrogen content may be neglected, are represented by points on the H/C axis. Thus, $(1.75, 0)$ corresponds to a structure in which there is one ring closure for every eight carbon atoms. The pencil of rays connecting this point with the $f_a = 1$ boundary represents a series of structures which contain one non-aromatic ring for every eight non-aromatic carbon atoms. In this regard, it may be noted that an olefinic double bond may be considered as a two-membered ring.

(4) Polymers of aromatic hydrocarbon units are represented by points on the line $f_a = 1$. One point may represent many different structures; for instance, $(0.5, 1)$ represents the following among others:



If R is the number of rings in a ring cluster, and C_R the number of carbon atoms constituting those rings, then the degree of compactness of the ring system may be defined as R/C_R ; the various ring systems above have the common property $R/C_R = 1/4$. Values of this ratio are shown on the $f_a = 1$ boundary in the figure.

(5) In all hydrocarbon systems for which the equation $f_a = 2 - H/C - 2R/C$ is valid, it is evident that in the f_a versus H/C diagram a family of straight lines with slope -1 may be drawn in which each line corresponds to a value of $2R/C$. A series of such lines is shown on the figure (p. 63) for $2R/C = 1, 2/3, 1/2$ and $1/3$. The term $2R/C$ has been called the ring index, or ring condensation index, by van Krevelen; it is a measure of the degree to which the carbon atoms are linked together into rings, and it is only indirectly connected with the degree to which those rings are fused into clusters or with the degree of compactness within the clusters. Thus, the straight line connecting $(2, 0)$ and $(0.416, 1)$ represents a series of infinite hydrocarbons consisting of aliphatic groups and coronene-type units. In this latter series, as the proportion of aliphatic material decreases the ring condensation index increases, although the size and internal compactness of the clusters of rings do not vary.

(6) Before the most meaningful conclusions may be drawn from consideration of the relationship of points representing real finite molecules to a background of lines representing series of polymers or structural units, it is necessary to apply a correction to the H/C ratio of those substances in which the contribution of the terminal hydrogen atoms cannot be neglected. This involves the adjustment of the H/C ratio by an amount equal to removal of two hydrogen atoms from each molecule. At a molecular weight of 500 this change in H/C is 0.04, at 1000 it is 0.02, and at 2000 a negligible 0.01. The necessity for adjusting the H/C ratio to a common structural basis before plotting reflects the difference between the composition equations:

$$H = 2C - C_A - 2R + 2 \quad (i)$$

$$\text{and } H = 2C - C_A - 2R \quad (ii)$$

Equation (i) applies to hydrocarbon molecules, and equation (ii) applies to hydrocarbon structural units with a functionality of 2.

The matter of correcting the hydrogen content of real substances is further complicated by absence of information on the mode of combination of hetero-atoms in the structure; nevertheless, it is instructive to plot the uncorrected H/C ratio of naturally occurring substances on the diagram.

(7) Consider points in the diagram lying within the area bounded by $H/C = 0$, $f_a = 0.75$, $f_a = 0.25$, and the line joining (0.5, 1) to (1.5, 0). The compositions represented by such points may be made up in a wide variety of ways which may be divided into three major types:

- (a) a physical mixture of molecules of very different chemical class, such as condensed polynuclear aromatic compounds and long-chain saturated hydrocarbons;
- (b) molecules which contain large segments of very different chemical class;
- (c) molecules which contain highly strained or unstable structures.

It is improbable that materials of type (c), composed of highly strained molecules or of structures containing olefinic or acetylenic multiple bonds, would survive geological processes and remain in a natural deposit at moderate temperatures.

In natural deposits of hydrocarbon materials the production of aromatic rings has resulted from processes, such as elimination of foreign atoms and hydrogen, which require conditions quite different from those required by processes leading to saturated paraffinic structures. The production together, in a deposit, of condensed polynuclear aromatic ring systems and large saturated paraffinic groups is therefore unlikely to have taken place,

either with the two types of structure combined in molecules as in (b), or separately as in (a). Further, groups that form junctions between aromatic and saturated parts of hydrocarbon molecules are often the most reactive sites in the molecules, and fission of the molecule is more likely to occur there than elsewhere. In a substance of type (b), the rupture of a few bonds at such sites would result in a substance of type (a). In deposits which have been subjected to processes of selection--such as extraction and concentration, or preferential reaction and destruction-- materials of type (a) are not likely to occur.

It would therefore be surprising if geological samples of hydrocarbons, or near-hydrocarbons, of high molecular weight had properties corresponding to the area of the f_a versus H/C diagram specified at the beginning of this section. Also, in any high-molecular-weight hydrocarbon corresponding to a point on or close to the H/C axis at an H/C value of less than about 1.5, any chemical reaction represented by a shift away from the H/C axis is likely to be catastrophic, the stability of the material decreasing as reaction proceeds. This area of the f_a vs H/C diagram is therefore unlikely to correspond to materials in natural deposits. Diamond corresponds to (0, 0) in the diagram, but it is a special case.

For these reasons, it is probable that hydrocarbon or near-hydrocarbon materials of high molecular weight, occurring in natural deposits, will correspond to points on the f_a vs H/C diagram within a band near the $f_a = 1$ boundary and the line $f_a = 3/4 (2 - H/C)$.

(8) Consider the slopes of the lines connecting (2, 0) and any two points representing real substances (after adjustment of H/C as in 6 above). In general, the point on the line of smaller slope (a greater negative value) represents a substance containing either less compact aromatic ring clusters, or a lower degree of cyclisation in its non-aromatic parts, than the substance represented by the point on the line of greater slope.

In the special case in which two substances have the same degree of ring-closure in their respective non-aromatic parts, and have aromatic parts of the same average compactness, a straight line may be drawn through the two points representing these substances to intersect the H/C axis and the boundary $f_a = 1$. From the co-ordinates of these two points of intersection it is possible to determine the degree of compactness, R_A/C_A , of the aromatic ring clusters of the two substances, and also the degree of ring closure among their non-aromatic carbon atoms -- this latter value is, in fact, the ratio of the number of non-aromatic rings to the number of non-aromatic carbon atoms.

(9) Figure 5 of the main section of this report shows points corresponding to the properties of various materials. For the purposes of this appendix the H/C ratios should be adjusted to a basis of a bifunctional polymer of infinite molecular weight, as in (6); this would make a slight difference

to a few of the points representing lower molecular weight samples.

That section of the 'adjusted' curve which is beyond an H/C value of about 1.5 cannot represent structures composed only of aromatic and aliphatic groups, since the lines joining (2, 0) and points on this section of the curve intersect the $f_a = 1$ boundary, either in the imaginary region where H/C is less than zero, or in the region requiring average aromatic structures to be large clusters of compactly fused rings. Other properties of these materials show that the average aromatic structures that they contain are not of this type, and it must be concluded that these materials contain considerable proportions of naphthenic structures.

A line from (0.54, 1) to (1.88, 0) represents a series of infinite hydrocarbons in each of which there is one non-aromatic ring for every 16.6 non-aromatic carbon atoms, along with aromatic ring systems of average degree of compactness $R_A/C_A = 0.23$. Between H/C values of about 1.6 and 1.0, the curve representing the geological samples lies close to this line; this allows the possibility that the samples may constitute a series in which the compactness of the aromatic ring system is only a little greater in samples of H/C = 1.0 than in those of H/C = 1.6, and the degree of ring closure in the non-aromatic parts only a little less. A greater f_a may then be accounted for either by the presence of larger ring systems with the same average degree of compactness as those in samples of smaller f_a , or by the existence of a greater number of separate ring systems of similar size and compactness to those in the less aromatic material. The value $R_A/C_A = 0.23$ is very close to that of the kata-condensed pentacyclic aromatics such as pincene and pentacene, and not far removed from 0.25, the value characteristic of a vast range of polycyclic aromatic ring systems, as noted in (4). A value of 4 for the reciprocal (C_R/R) of this ratio is a common assumption, in structural analysis schemes, for the average number of ring carbon atoms per ring in petroleum fractions.

This interpretation of Figure 5, the f_a vs H/C diagram of the section 'Aromaticity and the Ring Condensation Index' (page 23), is in harmony with the interpretation presented in that section (page 26) and with the results of the estimation of aromatic ring cluster size (pages 30-31).

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