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A GEOCHEMICAL EVALUATION OF HYDROCARBON
CHARACTERISTICS AS CRITERIA FOR THE ABIOGENIC
ORIGIN OF NATURALLY OCCURRING ORGANIC MATTER

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A GEOCHEMICAL EVALUATION OF HYDROCARBON CHARACTERISTICS

AS CRITERIA FOR THE ABIOGENIC ORIGIN OF NATURALLY

OCCURRING ORGANIC MATTER

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

The search for chemical evidence of prebiological processes in ancient and extra-terrestrial geologic samples has led to the need for criteria which can be used to distinguish organic matter of abiogenic and biogenic origin. A review of the types of hydrocarbons reported in the literature to be synthesized from simple carbon containing gases suggests that at least four hydrocarbon characteristics have potential as criteria: (1) A complex mixture of predominantly cyclic aliphatic hydrocarbons which yield a hump-like gas chromatographic distribution pattern, (2) a repetitive sequence of monomethyl branched paraffin and olefin isomers in between intense n-alkane peaks, the intensity of all peaks decreasing exponentially with molecular weight, (3) a mixture of two and three ring arenes consisting of even numbers of carbon atoms, and (4) a positive correlation of the C/H ratio of all hydrocarbon types with temperature of formation. This survey also suggests that the relative distribution of hydrocarbon types in an abiogenic mixture can provide information about the conditions under which it was synthesized. For instance, the first listed characteristic appears to indicate that methane was the reactant, while the second indicates carbon monoxide.

The usefulness of the aliphatic hydrocarbon characteristics in determining the origin of bitumens in unusual geologic environments is evaluated. A survey of bitumens from New Almaden Mine, California; Yellowstone National Park, Wyoming; Mountsorrel, England; and Asphalt Lake, Trinidad suggests that complex mixtures of predominantly cyclic aliphatic isomers are common to most of these unusual bitumens, yet there is evidence that they are of biological origin. To determine what processes could generate these isomer mixtures in biologically derived material, a bitumen deposit in Windy Knoll, England was studied in detail. Here the bitumens are directly associated with lead-zinc ore deposits and

previous studies of the area suggest that they have been thermally altered.

Three distinct bitumens were identified. One, a brittle brown solid, contains hydrocarbons very similar to those of the overlying shales. The other two, a viscous oil and a brittle, black solid, contain hydrocarbons exhibiting the complex distribution pattern observed in the previously surveyed bitumen deposits. Since the hydrocarbons isolated from associated, massive fluorite deposits were almost identical to those of the underlying limestone and overlying shales, alteration of the hydrocarbons due to hydrothermal activity or water transport is considered unlikely. On the basis of the indirect evidence of a high nitrogen content, presence of unsaturated hydrocarbons, and suitability of the environment for bacterial growth, it is suggested that selective bacterial oxidation of the aliphatic hydrocarbons is the main process responsible for the complex hump-like alkane distribution patterns at Windy Knoll. A geologic history for the deposit is postulated, which involves a two phase introduction of bitumens. Each phase is suggested to have begun as a pulse of warm saline fluids migrating along the shale-limestone unconformity passed through the topographic high at Windy Knoll. Microbial oxidation of the bitumens may have taken place during the deposition process or more likely as a recent, secondary oxidation process.

On the basis of the Windy Knoll study, it is concluded that there are subtle differences between altered biogenic and abiogenic aliphatic hydrocarbons. These differences make it possible to use their characteristics as an indicator for the abiogenic origin of organic matter especially if there is no evidence for bacterial activity in the samples. The information obtainable from the characteristics of the hydrocarbons in the Murchison carbonaceous chondrite is given as an example of how the results of this study can be applied.

CHAPTER 1

INTRODUCTION

Chemical Evidence for Life in Ancient and Extraterrestrial Rocks

Organic geochemistry began with man's first attempts to relate the chemical constitution of petroleum to various biologic and inorganic sources. From this search for the origin of petroleum emerged the concept that the presence of certain compounds such as porphyrins (Treibs, 1934) or certain characteristics such as a low C^{13}/C^{12} carbon isotope ratio (Silverman and Epstein, 1961) was a useful indication of the biogenicity of the host organic mixture.

A new phase of organic geochemistry evolved as attempts were made to find evidence in rocks that defined the time at which life began on earth, and the extent to which it occurred in our solar system (Ponnamperuma, 1965). These new quests extended geochemical studies to early Precambrian rocks and carbonaceous chondrites. Study of both types of samples placed new and stringent requirements on the type of markers which might serve to indicate the biogenic origin of the associated organic matter: for instance, the presence of amino acids is not a good criterion because amino acids are readily synthesized in electric discharges through methane, ammonia and water (Miller, 1953). Optical activity would be a better criterion, but it is difficult to detect when the amount of material is small (Hayatsu, 1966).

A promising new class of biological markers gained prominence at this time: hydrocarbons with the isoprenoid structure (McCarthy and Calvin, 1965). Their acceptance was based on the facts that hydrocarbons are the most stable of organic compounds, that instrumental techniques are available for their complete characterization on the microgram

level, that they are present in one form or another in a wide variety of plants and animals, and that they had not been synthesized in any chemical evolution model experiments. The search for these compounds in Precambrian rocks by several groups of highly skilled analytical chemists revealed the presence of open chained and cyclic isoprenoids in all major Precambrian rocks (Barghoorn, et al., 1965; Oro and Nooner, 1967; Belsky, et al., 1969; Han and Calvin, 1969) and in carbonaceous chondrites (Hayes, 1969). By this time, it appeared certain that life had existed as far back in the earth's history as 3.2 billion years, and that the evolutionary process must have been initially very rapid.

This intensive search for remnants of life in rocks generated several problems concerning the interpretation of this type of chemical evidence. It is generally acknowledged that chemical evolution preceded the evolution of biological systems (Ponnamperuma, 1964). Therefore it seems reasonable to expect that there might exist rocks old enough to contain abiogenically formed organic matter. Would the absence of isoprenoids characterize such material? Precambrian rocks containing abiogenic material could plausibly also contain chemical remnants of an emerging biological system. Would such a "contaminated" mixture be recognized?

At first, the most direct way to answer these questions appeared to be the development of abiogenic markers analogous to biogenic markers, by identifying stable hydrocarbons which do not occur in living systems, but which can be synthesized in hypothetical chemical evolution models. This solution never gained importance because normal diagenesis of biological compounds generates many entirely new isomers. For instance, the hydrocarbon, adamantane, found in petroleum (Landa and Machacek, 1933) is not present in living systems. This point raised another: could biogenic material undergoing diagenesis or some other form of alteration lose the characteristics which distinguish it from abiogenic matter?

A better approach to the problem of identifying naturally occurring abiogenic organic matter appeared to lie in the study of material synthesized in various chemical evolution

experiments, and in the development of characteristics which were not dependent on the presence or absence of a specific compound. And, indeed, initial studies showed that synthetic, aliphatic hydrocarbon mixtures yielded a hump-like distribution pattern upon gas chromatography which was very distinct from those of most sediment derived aliphatic hydrocarbons. Even more promising was the finding that the aliphatic hydrocarbons isolated from a bitumen reported in the literature as abiogenic were distributed in a manner very similar to the synthetic analogues (Ponnamperuma and Pering, 1966).

In spite of the unanswered questions, there was a brief period of time when it appeared that organic geochemistry had achieved its goals: traces of life in the earth's oldest rocks had been found, and some means to distinguish organic matter of biological and abiological origin had been developed. But no sooner had this goal been reached, than accumulating evidence based partly on geologic considerations began to erode the credibility of these findings.

Amino acids in recent sediments were found to racemize at such a rate that they would be racemic in about two million years (Kvenvolden and Peterson, 1970). Yet amino acids in Precambrian rocks were optically active (Kvenvolden, Peterson and Pollack, 1969). Permeability studies showed that enough water could flow through Precambrian rocks to introduce all the observed organic constituents (Smith, Schopf and Kaplan, 1970). In addition, the mobility of isoprenoids was demonstrated by the detection of these compounds in a wide variety of graphites (Gelpi, Nooner and Oro, 1970a), in dust (Gelpi, Nooner and Oro, 1970b), and in the outer layers of a meteorite which hit the earth only twenty-four hours previously (Han, Simoneit, Burlingame and Calvin, 1970). The use of isoprenoids as the sole criterion for the biogenicity of a sample was further questioned when these isomers were formed in several abiogenic syntheses (McCarthy and Calvin, 1967; Munday, Pering and Ponnamperuma, 1968; and Studier, Hayatsu and Anders, 1968). The validity of using hydrocarbons to characterize abiogenic material came into

further doubt when the apparently abiogenic bitumen was found to be optically active (Pering, unpublished results).

Two important points emerged from this period of intense analytical work. One was that the chemical differences between biogenic and abiogenic hydrocarbons are very subtle and still needed to be defined. The second was that the significance of any organic compounds in rocks must be interpreted in close conjunction with all available information about the geologic environment in which they are found. As these points were becoming apparent, this thesis study was undertaken.

Plan of Thesis

The primary purpose of this thesis is to define some of the characteristics of hydrocarbons which can be used as criteria for abiogenicity. An important part of the study is to determine how biologically derived hydrocarbons develop abiogenic characteristics.

There are four parts to this study. The first, presented in Chapter II, is a review of the types of hydrocarbons which can be synthesized from simple carbon containing gases. This review provides a basis for formulating the characteristics which are potentially useful as criteria for abiogenicity. In addition, the energy conditions employed in these syntheses provide a basis for defining favorable geologic environments for the formation of abiogenic hydrocarbons. The second, Chapter III, presents a series of brief studies of several bitumens selected from those reported in the literature as possibly abiogenic. These studies were carried out to determine whether any of the experimentally defined abiogenic characteristics were unique to these natural materials. The third and most extensive aspect of the study, presented in Chapter IV, is a survey of the hydrocarbon distribution patterns in a bitumen deposit whose genesis appears linked with hydrothermal mineralization processes in the surrounding sediments. Its purpose is to determine what natural processes will alter the biogenic characteristics of sediment derived, hydrocarbons so that they resemble abiogenic

material. The last and concluding part of the thesis summarizes the characteristics which appear to be the most valuable as criteria and discusses these characteristics in the light of those exhibited by the hydrocarbons in the recently fallen Murchison carbonaceous chondrite.

CHAPTER II

SYNTHESIS OF ABIOGENIC HYDROCARBONS

Introduction

The non-biologic processes by which hydrocarbons can be synthesized may be either equilibrium or non-equilibrium processes. In nature, equilibrium processes are important in systems such as those associated with the atmosphere at high temperatures, the solar nebulae, rock metamorphism, and vulcanism. The types of hydrocarbons which would be formed under such conditions have been predicted by Dayhoff and Eck (1966) on the basis of the free energies of selected compounds. For a system containing C, H and O they predict that methane is the dominant low molecular weight hydrocarbon formed, and that aromatic hydrocarbons will predominate by as much as 10^{20} over paraffinic hydrocarbons, if hydrogen is depleted in the system.

But many geologic processes involve predominantly non-equilibrium reaction. A meteorite hitting the earth, for instance, would not have time to equilibrate. The types of hydrocarbons which would be formed in these environments will thus differ from those predicted by Dayhoff and Eck, and are best defined by laboratory syntheses utilizing the various possible energy sources available within our solar system (Ponnamperuma, 1964). This section is a review of these reactions as observed in the laboratory. It has a dual purpose: to define the characteristics of synthetic hydrocarbons as potential criteria for the abiogenicity of naturally occurring bitumens, and to specify the most favorable conditions for the non-equilibrium synthesis of hydrocarbons on earth.

Types of Hydrocarbons Synthesized

Aromatic Hydrocarbons

Considering the thermodynamic stability of polynuclear aromatic hydrocarbons (Dayhoff, Lippincott and Eck, 1964), it is not surprising that they are formed in a variety of high energy syntheses, where reactions can proceed rapidly in both directions. Simulated cosmochemical synthesis involving passage of methane over silica gel at 1000° C produces mainly one, two and three ring arene hydrocarbons (Oro and Han, 1966); and the discharge of high intensity arcs through methane to simulate lightning produces a similar, but less condensed set of compounds which include benzene and toluene (Ponnamperuma and Woeller, 1964). In another cosmochemical simulation experiment, carbon monoxide and hydrogen heated to 900° C in the presence of powdered meteorite produces a wide range of aromatic compounds including pyrene and naphthalene (Studier, Hayatsu, and Anders, 1968). There is even some indication that calcium carbonate may react to yield polynuclear aromatics when heated to 500° C under high hydrogen pressures (Giardini, Salotti and Lakner, 1968).

The temperature range favorable to the formation of aromatic compounds is relatively restricted. This is probably because formation of these compounds involves the high energy methine (CH) radical which apparently does not appear below 700° - 800° C. At temperatures above 1000° C carbon, hydrogen and acetylene become the dominant products. Very high temperatures do not necessarily mean that aromatic hydrocarbons will not be formed, however, because acetylene will polymerize if it is cooled slowly through 1000° C. Such a process may explain the fact that the hydrocarbons formed upon passing methane through silica gel at 1000° C are composed almost completely of even numbers of carbon atoms (Oro and Han, 1966).

Aliphatic Hydrocarbons

Saturated.–Free energy calculations have shown that aliphatic hydrocarbons are not thermodynamically stable in any hydrogen deficient system (Eck, et al., 1966). This is reflected in the fact that aliphatic compounds are formed only in low energy, non-equilibrium syntheses. Corona discharges through methane, which simulates a possible primitive earth situation, produce acyclic and mono-cyclic hydrocarbons containing a large number of short chain branches (Ponnamperuma and Woeller, 1964). The gas chromatographic distribution pattern exhibited by these aliphatic hydrocarbons re-sembles a Gaussian distribution curve because the number of isomers is so great that they are not resolved on existing columns (Ponnamperuma and Pering, 1966). A very similar mixture of aliphatic hydrocarbons is produced when solid methane is irradiated with Cobalt 60 rays at 77° K in a simulated Jovian process (Davis and Libby, 1964). The average number of carbon atoms in the hydrocarbons formed in both of these syntheses is about fifteen, but the number varies inversely with the temperature of the reaction in the latter experiment.

A much different set of aliphatic hydrocarbons is produced by the reaction of carbon monoxide and hydrogen at moderately low temperatures, in the well known Fischer-Tropsch synthesis (Asinger, 1968). This synthesis can be summarized by the equation:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
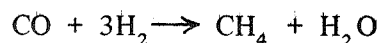
It has been frequently noted that long chain, aliphatic hydrocarbons can be formed in large yields in this reaction (McCarthy, 1968). An example of this reaction which may have some relevance to possible geologic processes is the use of hematite at temperatures of 200° to 325° C to polymerize these gases into predominantly straight chain, high molecular weight hydrocarbons containing some mono-branched and multi-branched isomers (Asinger, 1968). Similar hydrocarbons are produced when powdered meteorite is used as a catalyst at temperatures below 300° C (Oro, 1970). In the Fischer-Tropsch synthesis, temperatures

much above 300° C produce increasingly smaller molecular weight hydrocarbons no matter what the catalyst is. Below this temperature, catalysts are the main determinant of the type of compounds formed. For instance, if potassium carbonate is mixed with the hematite catalyst, the reaction products consist of high molecular weight alcohols, ketones and acids, and only two percent hydrocarbons.

Irradiation of methane by ultraviolet light at wavelengths below 1450 A° is another non-equilibrium process by which aliphatic hydrocarbons are synthesized. Low molecular weight hydrocarbons including ethane, ethylene, acetylene, propylene and minor amounts of five to six carbon containing molecules are formed *via* such reactions as:

$$CH_4 + hv \longrightarrow \cdot CH_3 + H\cdot$$
$$\cdot CH_3 + hv \longrightarrow \cdot CH_2 + H\cdot$$
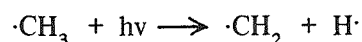
(Noyes and Leighton, 1941; Mahan, 1962; and Magee, 1963). It has been proposed that such reactions should lead to the formation of high molecular weight hydrocarbons, but this has not yet been shown experimentally (Lasaga and Holland, 1970).

Unsaturated.--Unsaturated isomers are a minor constituent of most synthesized hydro-carbon mixtures, as they tend to cyclize and form aromatic compounds, or polymerize. Acetylene, ethylene and propylene are about the only unsaturated compounds produced in significant amounts in high energy reactions such as in Tesla coil discharges through methane or methane, ammonia and water (Irving and Petterson, 1967); in the high temperature cracking of methane (Brooks, 1950); in the ultraviolet irradiation of methane (Mahan, 1962); and in the hydrolysis of metal carbides (Chang, et al., 1970).

Some larger olefins are formed by the pyrolysis of alcohols at temperatures of 350° C to 400° C (Brooks, 1950). This is probably the mechanism by which olefins are produced in the Fischer-Tropsch reaction. Their formation in this process is highly dependent on the ratio of carbon monoxide to hydrogen: a one to one ratio of these gases will yield 60%

olefinic hydrocarbons, but more hydrogen rapidly decreases this yield.

A process also relevant to the natural formation of olefins is the large scale industrial production of unsaturates in cracking reactions carried out above 500° C. An example of this process is the vapor phase cracking of gasoline at 600° C to form up to 50% unsaturated hydrocarbons (Brooks, 1950). Since rapid quenching of these products in most of these reactions is necessary to prevent auto-polymerization of the unsaturated compounds, a high thermal gradient is a favorable condition for their formation.

The importance of isoprenoids as biological markers in geological samples has generated considerable interest in the abiogenic synthesis of isoprene, the basic building block for these polymers. Attempts to identify isoprene in the methane discharge products were not successful (Ponnamperuma, 1969), and apparently the only way to synthesize dienes in large yields in geologically relevant processes is by selectively cracking a monoene (Brooks, 1950; McCarthy, 1968). For instance, butadiene is made by cracking butene at 654° C. An important constraint on this reaction, other than its starting out only with the monoene, is that it is very temperature sensitive: at 730° C only 2% butadiene is formed, and at 870° C, mainly hydrogen, methane and ethylene are produced. (Hydrocarbon mixtures such as those composing gasoline can be cracked to yield from 1% to 10% dienes, but these are usually butadienes rather than isoprene.)

Attempts to synthesize the structurally specific, linear 1,4-trans isoprene polymers have met with only limited success. Two possible pathways relevant to geologic processes have been proposed, both starting with isoprene as the reactant. One suggestion is that polymerization of the diene can take place on the surface of clays. And it has been shown that linear isoprenoid-like compounds are formed in preference to cyclic isomers when isoprene adsorbed onto vermiculite is irradiated with cobalt 60 rays, but the exact stereo-specificity of these products has not been determined (Munday, Pering and Ponnamperuma, 1968). The second proposal is that polymerization of isoprene occurs on a highly specific

catalyst such as $Al(Et)_3 - VCl_3$ in a non-aqueous solvent such as heptane (McCarthy and Calvin, 1969). However, the relevance of rare metal catalysts in non-aqueous phases to natural conditions is not clear.

Conclusions

Favorable Geologic Environments for Abiogenic Syntheses

This review suggests several characteristics of hydrocarbons that are potentially useful as criteria for abiogenicity. Before considering these, however, it seems judicious to first examine the geological significance of several aspects of these synthesis conditions. Perhaps the single most important condition necessary for hydrocarbon formation is that water (or oxygen) must be excluded or removed as it is formed.

Water is known to inhibit hydrocarbon formation in several ways, depending on the type of energy available for the synthesis. For instance, if ultraviolet radiation is the primary energy form, the water absorbs the energy necessary to cleave and form C-C and C-H bonds, and forms reactive species which compete or interfere with hydrocarbon synthesis in such reactions as:

$$H_2O + hv \longrightarrow H\cdot + OH\cdot$$

$$CH_4 + OH\cdot \longrightarrow \cdot CH_3 + H_2O$$
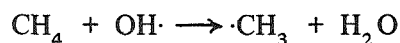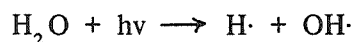
In electrical discharges, it has been shown that if water is present, the formation of hydrocarbons from methane drops from a total conversion rate of 43% to less than 4% (Irving and Petterson, 1967). Similarly, in corona discharges, the presence of water has been shown to result in the formation of carboxylic acids and other oxygenated material (Allen and Ponnamperuma, 1967). Even in the Fischer-Tropsch reaction, if water is not continuously removed as it is formed, the reaction products will be oxygenated. Thus, it appears that an important constraint on many geologic environments favorable to hydrocarbon synthesis (excepting carbide hydrolysis) is that they must be relatively anhydrous

or must contain "cold spots" where water may condense and collect.

This constraint has in the past often led to the conclusion that hydrocarbons *per se* could not be important prebiotic compounds, and that any abiogenic hydrocarbons indigenous to early Precambrian rocks would really represent geochemical degradation products of N- and O-containing primordial compounds rather than originally formed hydrocarbons. However, it seems as if there are at least two possible processes by which hydrocarbons could emerge and even become the dominant form for prebiotic organic matter on the nascent earth.

One process that has been recently proposed is that the reducing gases of the primitive earth concentrated in stratified layers as they were ejected from the interior of the planet (Lasaga and Holland, 1970). According to this hypothesis, methane and nitrogen would concentrate in the highest layers of the atmosphere. In this layer, the methane could react with ultra-violet light to form higher molecular weight hydrocarbons. These denser hydrocarbons would sink to lower levels in the atmosphere, and possibly collect on the earth's surface.

Another process not previously considered involves a sequential degassing of the earth. Current thinking suggests that water, methane, carbon monoxide, hydrogen, nitrogen and ammonia were degassed from the earth's interior as it heated toward the melting point of iron and began differentiating into a core, mantle and crust (Holland, 1962). The initial composition of these gases has traditionally been estimated as those that would be in equilibrium with silicate melts containing free iron. It seems possible, however, that the gases could have been generated in a non-equilibrium process, whose closest contemporary analogue would be the rapid metamorphism of water-rich rocks.

As the internal temperature of the earth increased, water released from initially hydrated silicates could have been transferred to cooler, outer portions of the earth where it would be assimilated to form new, stable silicate hydrates. The inert gases, such

as methane and nitrogen, which would be generated as metal nitrides and hydrides reacted with the released water, and which do not readily combine with either silicates or metals, could conceivably accumulate and be released to the surface of the earth. The net effect of retaining water in the earth as hydrated silicates would be an initially anhydrous primitive atmosphere. In this, hydrocarbons could form by polymerization induced by ultraviolet irradiation of simple hydrocarbon gases, or by thermal polymerization as meteorites hit the surface. As the planet heated to the point at which water could no longer be retained, it would be introduced into the atmosphere, but previously formed, relatively inert hydrocarbons would be preserved on the earth's surface or in its primitive waters. (See Appendix for calculations.)

Once the earth differentiated into a core, mantle and crust, and the atmosphere became oxidizing, conditions favorable to the synthesis of hydrocarbons become much more difficult to define. The experimental work previously outlined has suggested over the years three possible processes. The oldest is that carbides in magmas upwelling from the mantle would react with water to yield hydrocarbons, but this is unlikely because no carbides have been reported. A second possibility is that impacting meteorites could introduce organic matter into the now oxidizing earth's lithosphere. A third possible source of contemporary abiogenic hydrocarbons is fluid inclusions in minerals or rocks containing unstable radioactive isotopes such as uranium and thorium. It has been suggested that here, methane and nitrogen polymerize to form higher molecular weight hydrocarbons as they are bombarded with radioactive emanations (Kranz, 1968; Petersilye, 1964; Davidson and Bowie, 1951).

Possible Criteria for Abiogenicity

Turning now to the characteristics of hydrocarbons which could serve as abiogenic criteria, two factors important in their selection must be kept in mind: (a) the characteristics should be absent in biologically derived material, and (b) they should be consistently present in at least one type of synthesis products.

One characteristic seemingly compatible with these factors is the symmetrical, hump-like gas chromatographic distribution pattern exhibited by the aliphatic hydrocarbons synthesized from methane at moderate temperatures. Associated with this is the characteristic predominance of cyclic and highly branched nature of the aliphatic hydrocarbon isomers. Another distinguishing trait associated with the high temperature products of both methane and carbon monoxide is that the aromatic hydrocarbons are primarily unbranched and composed of even numbers of carbon atoms. The distribution pattern of the aliphatic hydrocarbons produced from carbon monoxide is also highly distinctive. This array of normal and branched isomers is marked by a rapid decrease in concentration versus hydrocarbon chain length, and by a regularly repeating sequence of methyl substituted paraffins and olefins between the major normal alkane peaks.

Finally, a characteristic suggested by all of the experimental data reviewed in this section is that there is a variation of hydrocarbon type with temperature of formation which is relatively independent of the reactant. This relationship can be seen in the increase of C/H ratio of the hydrocarbons with the estimated formation temperature. The resulting curve, shown in Fig. 1, reflects in large part the relative stability of the C–H bond (87.3 Kcal) and the C–C bond (58.6 Kcal).

The usefulness of all five of these characteristics in determining the origin of naturally occurring hydrocarbons seems at this point relatively promising. However, evidence presented in the next two sections indicates that the first two characteristics especially, must be interpreted with great caution.
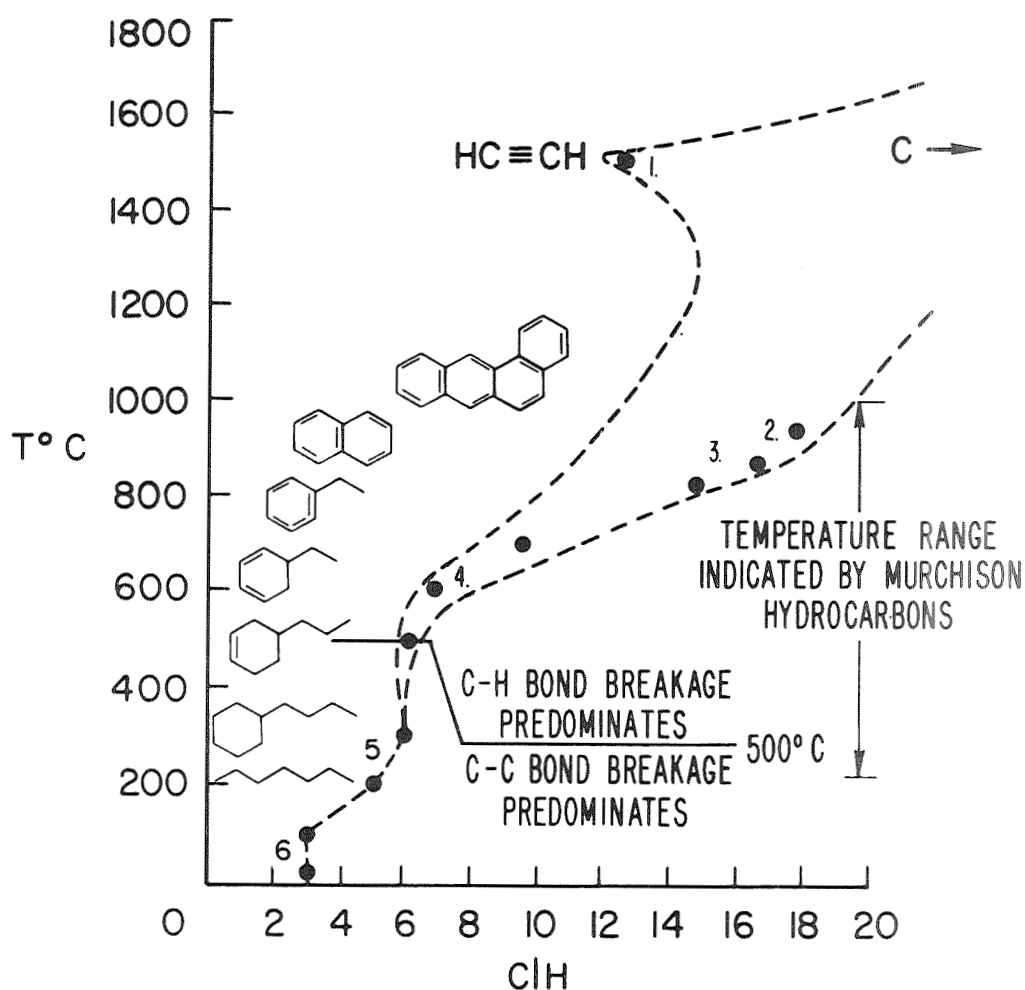
Fig. 1.–Variation of the C/H ratio of hydrocarbons with their temperature of formation as estimated from published results of non-equilibrium synthesis utilizing low molecular weight carbon containing gases. Structures illustrating the type of hydrocarbons represented by specific C/H ratios (black dots) are drawn in at various temperatures. The reference suggesting the placement of these specific ratios is listed below. The dashed lines serve only to give an idea of the range over which the C/H ratios appear to vary with temperature.

1. Friedmann, Bovee and Miller (1970
2. Oro and Han (1966)
3. Studier, Hayatsu and Anders (1968)
4. Brooks (1950)
5. Asinger (1968); Gelpi, Han, Nooner and Oro (1970)
6. Mahan (1962)

CHAPTER III

ABIOGENIC CHARACTERISTICS IN NATURALLY
OCCURRING HYDROCARBONS

Introduction

It has been shown in the preceding section that the hydrocarbons produced in synthesis experiments have some characteristics which theoretically could serve to define abiogenic hydrocarbons of terrestrial and extraterrestrial origin. Ideally, it should also be shown that these characteristics are unique to naturally occurring abiogenic bitumens and are not present in biological material in similar geologic environments. However most reports in the literature of abiogenic organic matter are highly subjective and are usually based simply on the association of the organic matter with some manifestation of igneous activity. An extensive study of every deposit would be required to unequivocally determine the origin of the bitumens, but this is beyond the scope of the thesis. Thus, this section is simply an attempt to measure the extent to which some of the experimentally defined abiogenic characteristics appear in the hydrocarbons isolated from these bitumens, along with the extent of the general chemical and geological evidence for their biogenicity.

The occurrences listed in Table 1 provide some idea of the variety of bitumens associated with hydrothermal mineral deposits. A brief explanation of why specific bitumens were not examined is included in this table.

Bitumens in Non-sedimentary Geologic Deposits

Mountsorrel, England

The first bitumen examined is associated with a Caledonian granodiorite complex in Mountsorrel, England, about seven miles north of Leicester. Five stages of mineralization

TABLE 1

SURVEY OF BITUMENS REPORTED TO BE ASSOCIATED WITH HYDROTHERMAL DEPOSITS

Type of Organics	Location and Host Rocks	Associated Inorganic Material	Postulated Geologic Source	Comments and Reference
Asphalt	Trinidad: Asphalt lake in Tertiary sandstone	clay, sand	mud volcano	see p. 24; Dauvillier (1965)
Solid, Black Bitumen	Norway: Hydrothermal Ag deposit; dolerite dike	calcite, silver, chalcopyrite, fluorite, chlorite	juvenile fluids from Permian granitic magma	negligible amount available; Dons (1956)
Viscous Brown Bitumen	England: Along contact of diabase dike with granodiorite	calcite, pyrite, chlorite, goethite, marcasite	hydrothermal fluids	see p. 76; Sylvester-Bradley et al. (1963), King (1959)
Fluorinated Compounds	Germany: Inclusions in fluorite and k feldspar	uranium oxides, fluorite	radiation induced polymerization	currently being studied by Kranz; Kranz (1968)
Gases, Solid Bitumen	Kola Peninsula, Russia; South Greenland: Ultra-basic and alkaline meta-morphic rocks	k feldspar, sphene, nepheline	polymerization of gases upon cooling	see p. 34; Petersilie (1964), Petersilie and Sorenson (1970) Borneman and Starynkevich (1933)
Solid Liquid Bitumen	New Mexico: Precambrian granite breccia	calcite	none	negligible amount available; Pratt (1961)
Solid, Liquid Bitumens	N. Derbyshire, England: Pb-Zn-Ba-F ore deposit in Carboniferous limestone	calcite, marcasite, fluorite, galena	hydrothermal fluids	see p. 36; Sylvester-Bradley, et al. (1963)
Petroleum	Terrestrial igneous rocks		upper mantle	no specific sample identified; Rudakov (1969)
Liquid, Solid Bitumens	Sulfur Springs, and New Almaden, Calif.: Froth veins with hydrothermal mercury Almaden, Spain: Hg in quartzite King Mine, Texas: Hg	opal, quartz, calcite, sericite, zircon	hydrothermal fluids	see p. 29; Sylvester-Bradley et al. (1963), Bailey (1959) Ransome (1921) Yates and Thompson (1959)
Liquid, Solid Bitumen	Yellowstone Nat. Park, Rainbow Springs and Calcite Springs: Hot water and steam	sulfur, calcite, gypsum	hot water interacting with oil	Love and Good (1969)

apparently affected the granodiorite (King, 1959): the last stage, which is thought to be part of the late Carboniferous-early Permian earth movements, involved the emplacement of a series of WNW-ESE trending diabase dikes in the granodiorite. The bitumen, along with calcite, dolomite and chlorite, is aligned along joints and fractures which generally parallel the contact of the diabase with the granodiorite, but in some places crosscut the dikes. Thus, bitumen deposition postdates both intrusion and solidification of the diabase. The bitumen has been described as ranging from a "mobile, oily liquid" to a more viscous tar which "gradually hardens on exposure to a black, pitch-like substance" (King, 1959). It is considered possibly abiogenic because of its association with igneous rocks (Sylvester-Bradley, et al., 1963).

Samples for study were obtained from the University of Leicester collection (R. J. King, sample curator). Most were in the form of chunks about 1-3 inches in diameter which were held rigid by the calcite matrix (Fig. 2). Fragments of the bitumen were manually separated from the calcite and analyzed by the usual procedure (see pages 72-75 for details). The alkanes, which constitute less than 1% of the total bitumen are predominantly saturated and yield a hump-like distribution pattern upon gas chromatography on various columns (Fig. 3). Mass spectra of these aliphatic hydrocarbons show that the dominant homologous series is C_nH_{2n-2}, which is the same as that of the methane discharge products (Ponnamperuma and Pering, 1966). The infrared spectrum of these aliphatic hydrocarbons shows strong absorption in the 720 cm-1 region (Fig. 4), indicating the presence of long chain methylene groups (Nakanishi, 1962).

Minute amounts of straight chain isomers are present in this bitumen. Attempts to isolate fractions from an SE-30 column, corresponding to the retention time of the iso-prenoid hydrocarbons, and re-injection onto a more polar column failed to detect these compounds. The aliphatic hydrocarbon, however, did show a net optical rotation of +1.54 (K. Pering, unpublished results, determined on a modified Beckman instrument). The

Fig. 2.--A fragment of the Mountsorrel bitumen showing the interlacing calcite.
Collected from Mountsorrel Quarry by R. J. King. (Photo by Ames Research Center)

Fig. 3.--Gas chromatograms of the aliphatic hydrocarbons isolated from the Mountsorrel, Trinidad, and North Derbyshire bitumens: (a, c) 50' S. C. O. T. OV-1 column, 2°/min., He flow 3 ml/min.; (b) 50' SE-30 column, 2°/min., He flow 3 ml/min.

(a) MOUNTSORREL BITUMEN

SOLVENT

100   150   200   250 HOLD

(b) TRINIDAD ASPHALT

100   150   200   250   300 HOLD

(c) NORTH DERBYSHIRE ELATERITE

SOLVENT

100   150   200   250 HOLD

TEMPERATURE °C
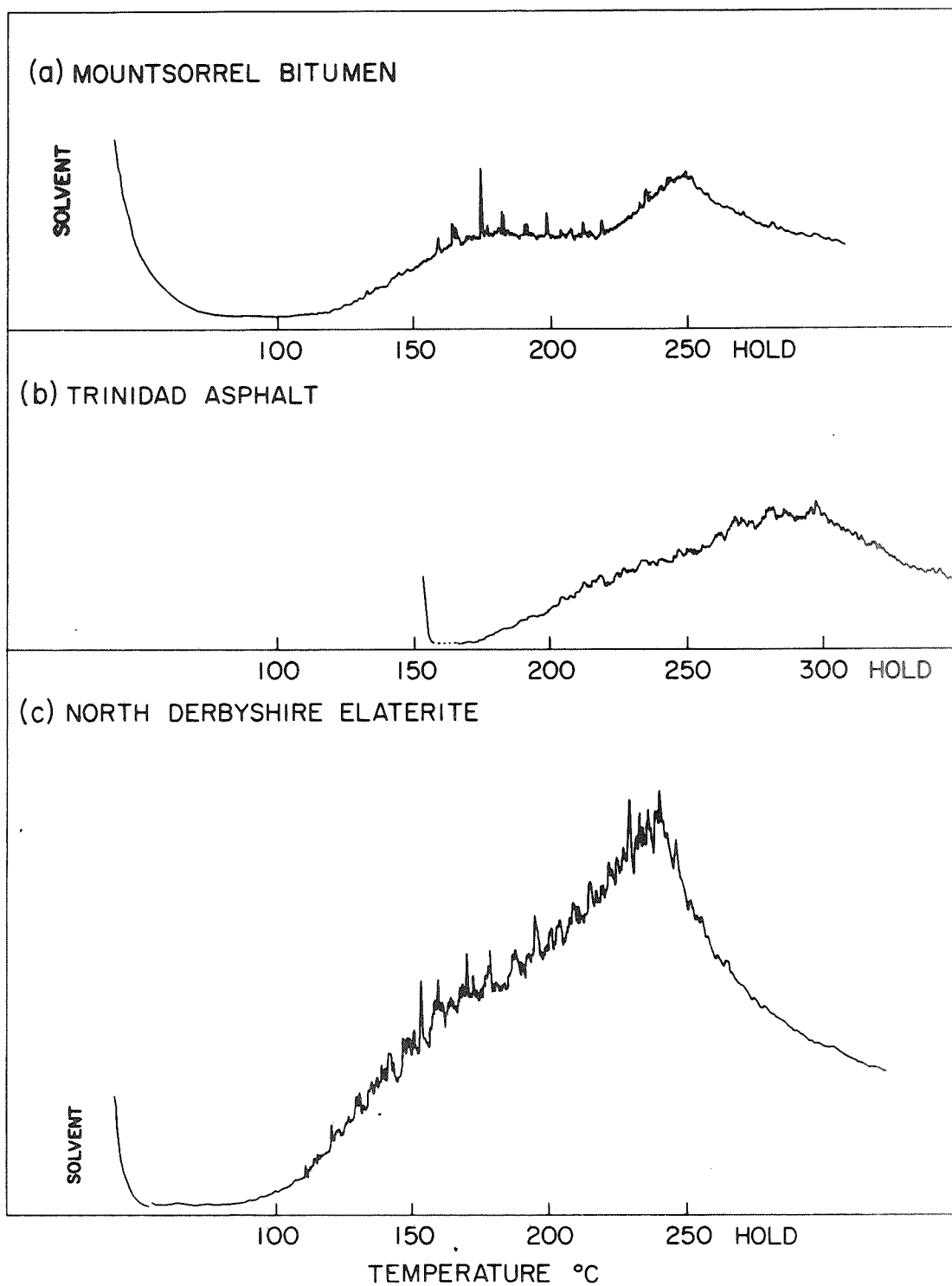
Fig. 4.–Infrared spectra of the aliphatic hydrocarbons isolated from:
(a) Mountsorrel bitumen, (b) Trinidad bitumen

A. MOUNTSORREL
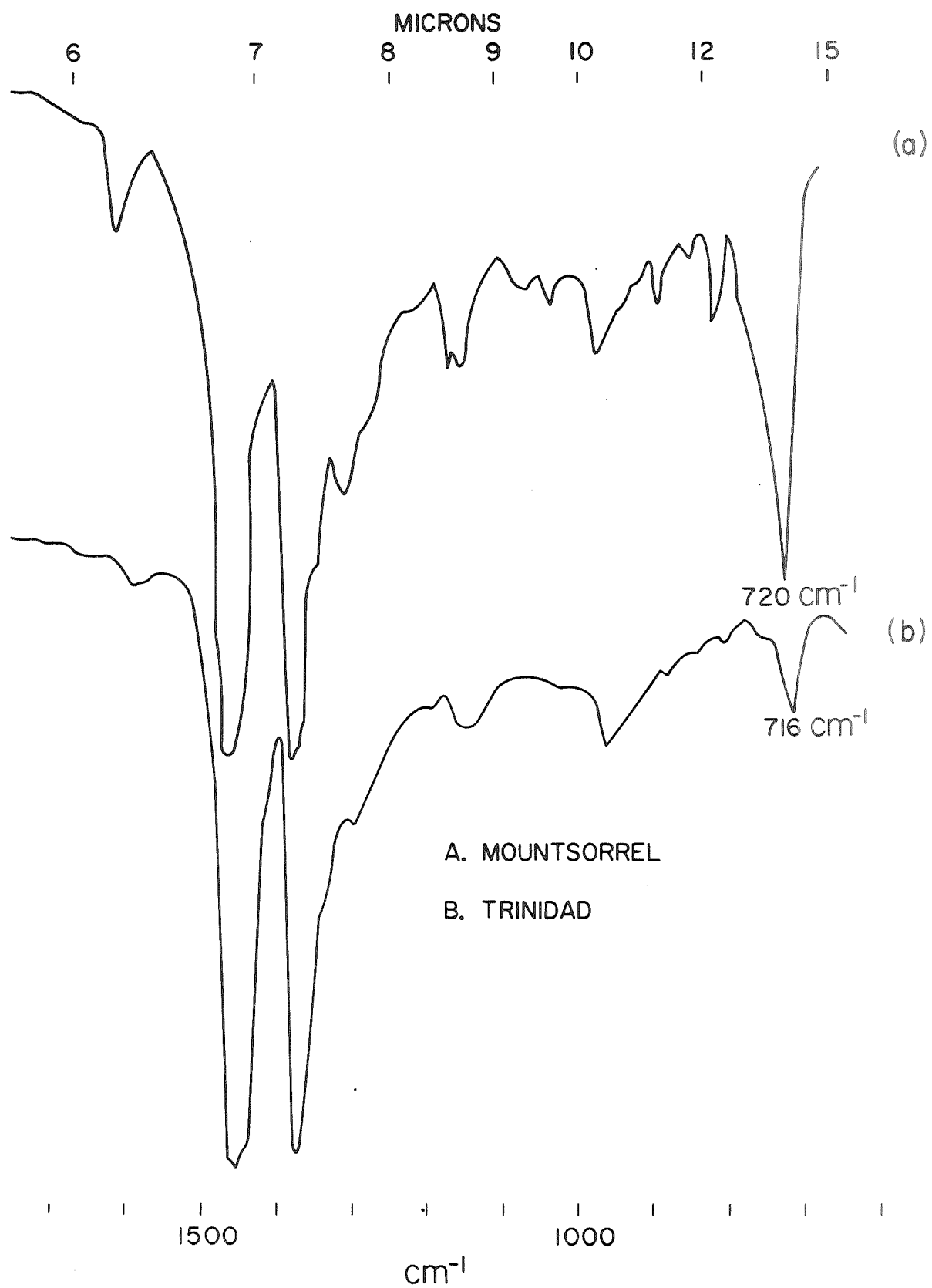
B. TRINIDAD

carbon isotope ratio of the material is typical of biologically derived material (S. Silverman, personal communication). Amino acids have also been detected in the bitumen (Aucott and Clarke, 1966).

Asphalt Lake, Trinidad

The source of the Trinidad asphalt has been clearly shown to be Tertiary strata (Suter, 1960). However, Duvallier (1965) considers the Trinidad asphalt an example of an abiogenic hydrocarbon mixture formed by volcanic processes. He presumably based this conclusion on the crater-like appearance of the asphalt lake, its characteristic bubbling motion, and the presence nearby of mud volcanoes. Because of these conflicting reports, this deposit was investigated in this study.

Samples of the asphalt were collected by C. Ponnamperuma. Analysis by the usual procedure showed that the aliphatic hydrocarbons constitute about 1% of the total bitumen, are predominantly saturated, cyclic and exhibit a hump-like distribution pattern (Fig. 3; see also Ponnamperuma and Pering, 1967). The infrared spectrum of the aliphatics shows only moderate absorption in the 720 cm^{-1} region, suggesting that long alkyl methylene chains are not prevalent. The aliphatic hydrocarbons isolated from the Naparima Shale, considered to be the source rock of the asphalt, gave a similar distribution pattern (sample obtained from K. Kvenvolden).

Aside from the probably sedimentary origin for the asphalt evidence for its biogenic origin includes the presence of large amounts of porphyrins (Macovei, 1938) and amino acids (K. Pering, unpublished results).

North Derbyshire, England

The third bitumen of ambiguous origin to be examined is from Windy Knoll in North Derbyshire, England. A comprehensive study of the area by G. Mueller (1951) led him to the conclusion that the variety of the bitumens in the area was the result of thermal

distillation of organic matter from sedimentary rocks by hydrothermal fluids. Later, ge-
ologists at the University of Leicester expressed doubts about his conclusions and raised
the question of its abiogenicity (Sylvester-Bradley, et al., 1965). The aliphatic hydro-
carbons in a sample of elaterite, one of the principal bitumens, were found to display a
gas chromatographic distribution pattern and infrared spectrum very similar to those of
the Mountsorrel alkanes. This area is studied in detail in Chapter IV.

Yellowstone National Park, Wyoming

Hydrocarbons have been observed in at least five thermal areas within Yellowstone
National Park (Love and Good, 1969). These are thought to be derived from Paleozoic
and Mesozoic sedimentary rocks underlying surficial Eocene to Pleistocene volcanic rocks.
Hot water and steam in this area apparently steam distilled the petroleum into the thermal
springs and vents. Bitumens emerging at Calcite Springs and Rainbow Springs were collected
for this survey.

Calcite Springs is located near the bottom of Yellowstone canyon in a sequence of
highly altered mafic tuff, conglomerate and basalt flows, collectively called the "Early
Basic Breccia." The hydrocarbons here are in a black bitumen which coats rhombohedral
sulfur crystals, or more rarely, alunite and gypsum, around the fumarole vents (Fig. 5).
The bitumen was extracted from the sulfur with benzene, and excess free sulfur removed
by passing it over colloidal copper (Blumer, 1957). The aliphatic hydrocarbons, isolated
by standard procedures, yielded a distribution pattern upon gas chromatography which is
characterized by a hump with superimposed peaks including those corresponding to normal
and isoprenoid isomers (Fig. 6).

At Rainbow Springs, located on Deep Creek in the northeastern part of the park, the
hydrocarbons are in the form of a pale yellow oil floating on the hot water. A sample of this
oil was injected directly into the gas chromatograph, yielding the chromatogram shown in
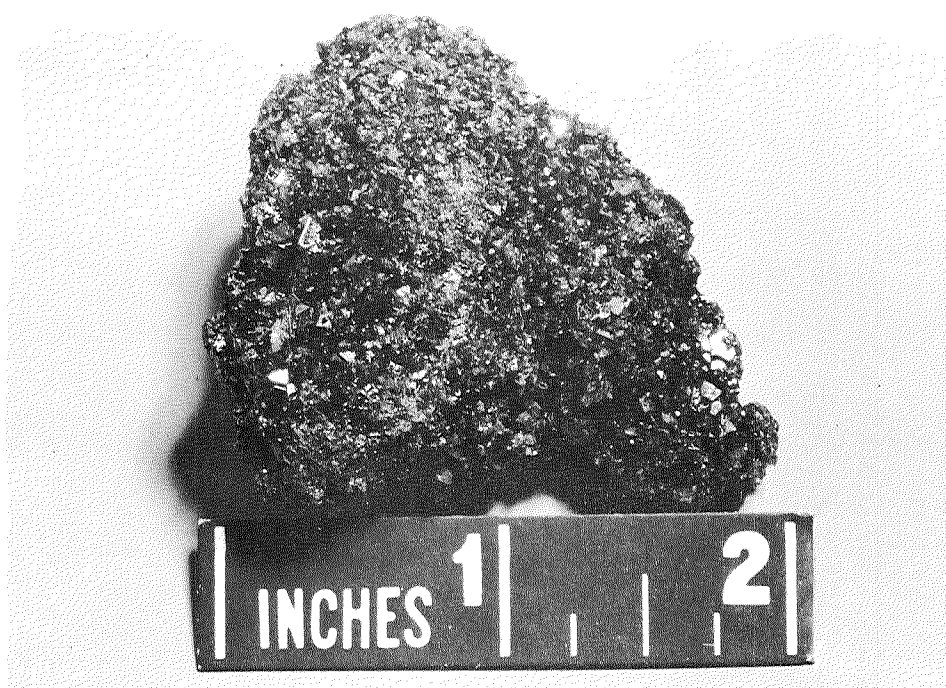
Fig. 5.--Black bitumen coating sulfur crystals (Photo by Ames Research Center), and black bitumen emerging from fumarole vents at Calcite Springs (Photo by K. L. Pering)

Fig. 6.–Gas chromatograms of the aliphatic hydrocarbons isolated from Calcite Springs and Rainbow Springs Bitumen. 50' OV-1 S. C. O. T. column; 2°/min, He flow rate 3 ml/min.

(a) RAINBOW SPRINGS

SOLVENT

(b) CALCITE SPRINGS

SOLVENT

TEMPERATURE °C

100   150   200   250 HOLD

28
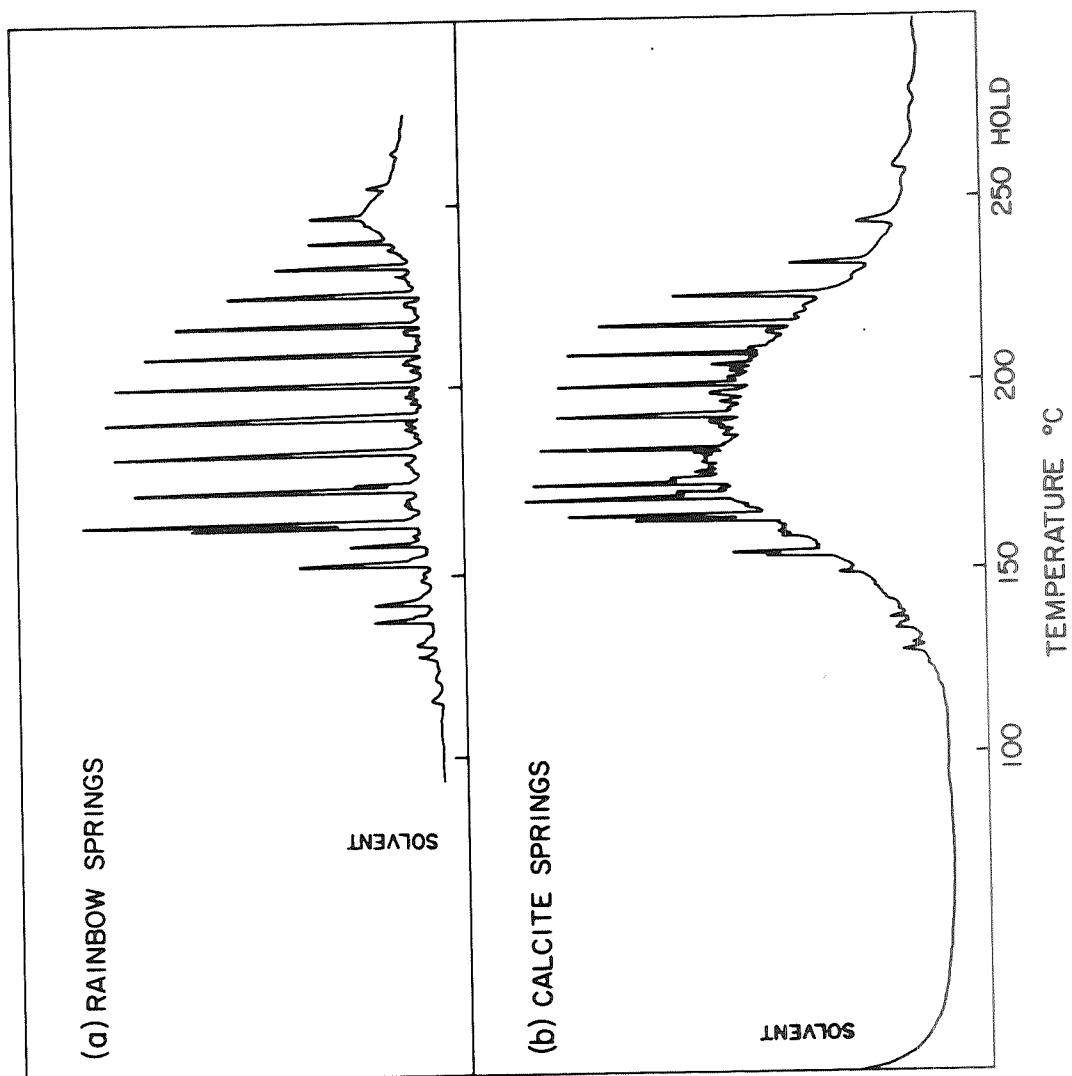
Fig. 6. Apparently, it is composed entirely of normal alkanes and some branched isomers.

New Almaden, California

The last bitumen examined is associated with the New Almaden mercury mine, located just south of San Jose, California. The New Almaden ore is emplaced in a shatter zone of Franciscan sandstone and shale, lying above and around a sloping peridotite intrusive contact (Bateman, 1942). The origin of the organic matter is unknown. Study of oil from the Sulfur Bank mine to the north suggests that the bitumens may be related to petroleum and oil from Cretaceous rocks a few miles east in the Sacramento Valley (Barnes, 1967). The bitumen at New Almaden is either a viscous asphaltic liquid, or a brittle solid which occurs in vugs often lined with quartz crystals (Fig. 7). The aliphatic hydrocarbons isolated by the usual procedure, yield a hump-like distribution pattern upon gas chromatography (Fig. 8).

Summary and Conclusions

This brief survey suggests that many of those bitumens associated with non-sedimentary geologic deposits contain aliphatic hydrocarbons which are not distributed like those in sediments (Breger, 1963). Hump-like distribution patterns similar to those produced by polymerization of methane are common to these alkanes. Furthermore, they are composed predominantly of cyclic isomers. However, these characteristics, which alone are suggestive of an abiogenic origin for these bitumens, are in conflict with concomitant chemical evidence (present in varying degrees in each bitumen) for biogenicity in the form of optical activity, isoprenoid isomers, and biogenic carbon isotope ratios. Furthermore, the deposits containing these complex hydrocarbon mixtures are composed largely of aromatic hydrocarbons. Yet there is no evidence that the genesis of these bitumens involved the high temperatures associated with abiogenic aromatic hydrocarbons. And, all the bitumens are associated with water rich geologic environments but it has
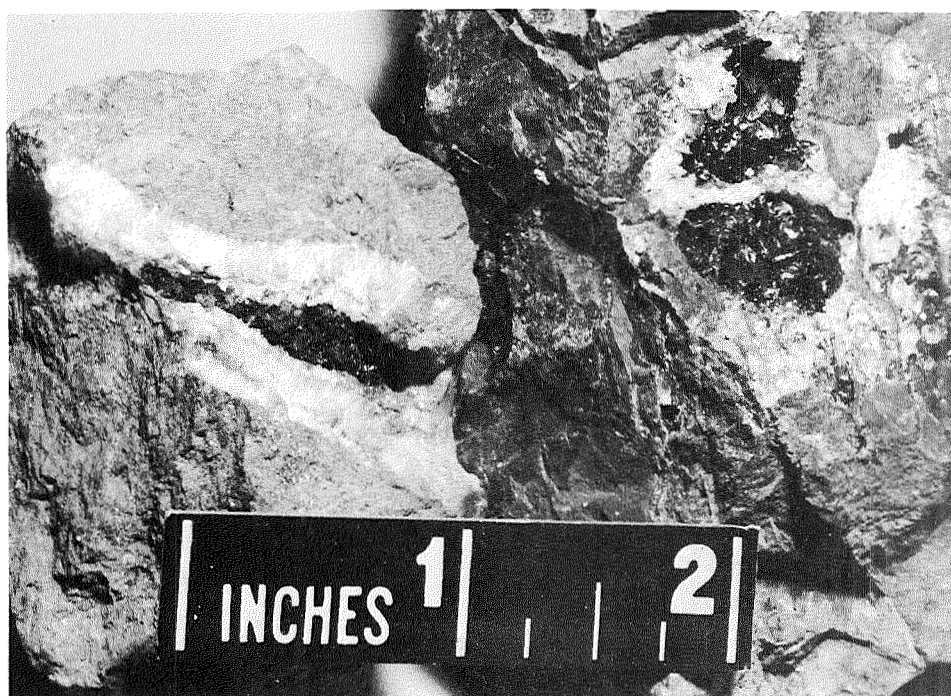
Fig. 7.--Weathered (left) and unweathered bitumen in silica-carbonate cinnabar ore, New Almaden Mercury Mine (Photo by Ames Research Center)
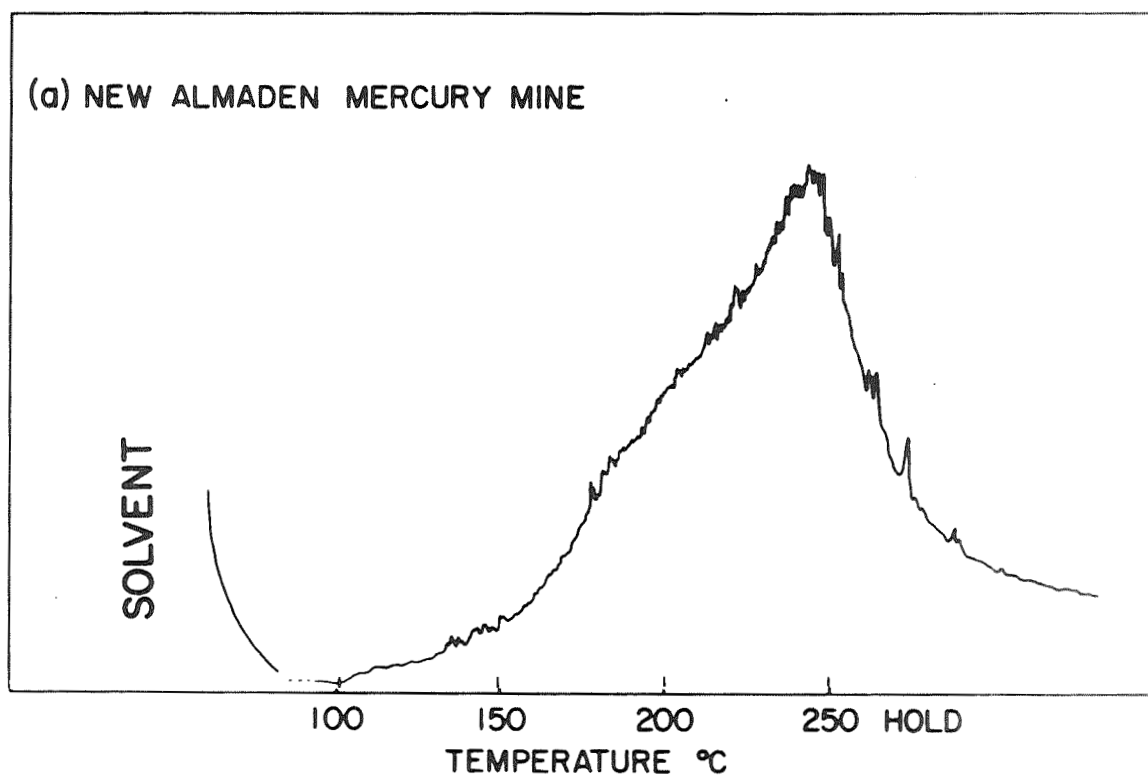
Fig. 8.–Gas chromatogram of the aliphatic hydrocarbons isolated from the
New Almaden Mine bitumen, same conditions as in Fig. 6

been shown that the presence of water inhibits hydrocarbon formation.

Apparently, the hump-like distribution pattern is too general a characteristic to be used as a criterion for abiogenicity unless different types of humps can be defined and associated with specific biogenic or geologic processes. Completely differentiating among the various types of humps ideally would require the complete identification of the various isomers composing the hydrocarbon mixtures. But the very fact that these mixtures cannot be resolved on available gas chromatography columns makes this task a very difficult one.

Fortunately, some general distinctions can be made between the aliphatic hydro-carbon mixtures. For instance, the humps found in the bitumens associated with hydro-thermal deposits are asymmetrical, almost bimodal in shape and reach a maximum in intensity in the high molecular weight (C_{25-30}) hydrocarbon region.

Another point of contrast is that these natural, biogenic bitumens yield aliphatic hydrocarbons which consistently have a higher proportion of methylene to methyl groups, in contrast to the methane polymerization products, which exhibit a large number of methyl carbons. (The large number of methylene carbons may be in the form of long chains as in the Mountsorrel bitumen, or of condensed cyclic structures as in the Trinidad bitumen.)

Much more difficult is the task of defining specific causes for these complex alkane mixtures. It is tempting to search for a process(es) that would explain the genesis of all the bitumens. And even though the geologic histories are widely disparate, their formation apparently involved some common conditions which might be clues to what these pro-cesses might be.

For example, all the bitumens, with the exception of the Trinidad asphalt, are asso-ciated with minerals deposited at moderately elevated temperatures. This suggests that thermal metamorphism of sedimentary organic matter might have generated the complex alkane mixtures. This explanation seems particularly pertinent with regard to mercury

deposits in California, as there is evidence that the waters associated with these are metamorphic waters derived from the Pacific Tectonic Belt (Barnes, 1970).

Another possible cause is suggested by the fact that all these bitumens have been transported to their present deposition site in a water rich fluid phase. It seems plausible that during transport of the organic matter, the more polar and more soluble aromatic constituents would travel the furthest and would preferentially carry alkanes similar to the aromatics, the cyclic isomers, instead of the normal or branched isomers (Welte, 1965). Some evidence for this process can be found in the Yellowstone bitumens if it is assumed that they are of the same origin, because one is highly aromatic and contains a large amount of unresolvable cyclic material, while the other is almost entirely paraffinic.

A further possibility is that chemical alteration of the organic matter takes place in the water independent of temperature or migration effects. This might involve oxidation decarboxylation, reduction, etc., of the organic matter to generate the hydrocarbons. This process is compatible with the seemingly puzzling fact that a complex aliphatic hydrocarbon mixture was isolated from the Trinidad source rock, as this finding suggests that alteration of the organic matter took place before or during deposition of the sediment.

Obviously, the evidence presented in this survey is far too scanty to do more than suggest possible alteration processes. It does emphasize that to clearly define these, a complete study of the geologic history of the host rocks, source rocks and chemical composition of each bitumen would have to be made. Such a study of one bitumen is attempted in the next Chapter. The results of this study will not explain the genesis of all complex hydrocarbon mixtures, but may help to eliminate some possibilities and provide concrete evidence for the effectiveness of others.

As mentioned earlier, there appears to be evidence that the bitumens examined in this survey are biological in origin. However, more work should be done on each deposit

to conclusively prove this. There are other bitumens such as the thucolites, not touched on in this study, which may still prove to be abiogenic, but it is very difficult to assess just how likely this possibility is from reports in the literature.

An illustration of the problem of assessing in advance the probability that a particular bitumen is abiogenic is afforded by the report of the recently hypothesized "abiogenic bitumens" disseminated in an alkaline intrusion in South Greenland (Petersilie and Sorenson, 1970). The twenty-eight rock samples from this intrusion, which include naujaite, sodalite foyaite, augite syenite, arfvedsonite lujavrite, and olivine gabbro, yielded upon extraction with chloroform, brown, liquid and solid bitumens. These bitumens are characterized simply as highly oxygenated naphthenic hydrocarbons with short chain substituents. Also observed in the rocks were large amounts of hydrocarbon gases (CH_4, C_2H_6, etc.) in the coarse grained rocks, hydrogen in the fine grained rocks, and little or no carbon dioxide or carbon monoxide.

The presence of the hydrocarbon gases instead of the usual carbon dioxide in these rocks is suggested to be due to Fischer-Tropsch type reactions in which the carbon dioxide reacts with hydrogen during metamorphism (or metasomatism) associated with emplacement of the lujavrite. The highly oxygenated state of the liquid and solid bitumens is considered due to oxidation of the original high molecular weight hydrocarbons presumably during the same metamorphism.

Disturbing questions are raised by these observations and associated explanations. Where did the hydrogen come from to reduce the carbon dioxide? How can a strongly reducing reaction occur simultaneously with an oxidizing one? Or to put this in a different light, why are the liquid and solid forms of carbon in an oxidized state while the gases are in a reduced state? Why is methane concentrated in the coarse grained rocks, the hydrogen in the fine grained, but the liquid and solids are evenly distributed? And yet, in spite of these questions, the only evidence upon which the inorganic origin of the organic matter

is based is: (a) the gases are present under pressure and (b) *one* measurement of a gas

sample yielded a δ C^{13} value (-.77) similar to that of magmatic carbon dioxide.

CHAPTER IV

ALTERATION PROCESSES AFFECTING HYDROCARBON DISTRIBUTION PATTERNS IN THE BITUMENS AT WINDY KNOLL, NORTH DERBYSHIRE, ENGLAND

Introduction

This portion of the thesis is a study of a deposit of organic matter in central England for the purpose of determining the effects of geologic processes other than sediment diagenesis which can alter organic matter and affect its hydrocarbon distribution patterns. Interest in this particular deposit was first aroused by study of samples of two of the bitumens sent to us from England in 1967. In these samples, striking differences were noted in the distribution of their aliphatic hydrocarbons, including the apparent loss of certain biogenic characteristics from one of them (Pering and Ponnamperuma, 1968).

A period of three weeks, from May 4 to May 30, 1968, was spent in Derbyshire collecting more bitumen, rock and mineral samples, as well as surveying the principal geologic features of the area under the guidance of local geologists. These samples were analyzed during the period 1969-1970, along with petroleum samples obtained from the British Petroleum Company.

Previous work on this area is confined to a doctoral thesis study of these and other bitumens in the North Derbyshire area (Mueller, 1951). Mueller considers the Windy Knoll deposit part of a highly differentiated hydrothermal vein system. Within the main vein he observed an ordered series of bitumens which he distinguished on the basis of their H:C and O:C ratios. The main bitumens were classified as follows:

1. Carbonite—black solid

2. Olefinite—brown solid

3. Ozocerite—hard wax

4. Viscous mutabilite—a turbid, light brown semi-solid

5. Elaterite—yellow-brown viscous liquid

6. Soft porous Mutabilite

7. Soft clear Mutabilite

After a detailed study of this deposit Mueller concluded that its geologic history involved three episodes of mineral deposition, two episodes of bitumen injection, at least one period in which the deposit was mechanically disturbed, and finally oxidation of the marcasite to produce SO_2 (Mueller, 1970). He interprets these observations and those that he made elsewhere in the area as evidence of hydrothermal alteration of "coal type" substances in the overlying shales. This alteration process he hypothesized involves the following sequence of events:

1. Hydrothermal fluids contacted the shale. Free hydrogen formed as coal-type substances in the shale were distilled and as water reacted with carbon to form carbon monoxide.

$$H_2O + C \longrightarrow CO + H_2$$

$$H_2O + CH_4 \longrightarrow CO + 3H_2$$
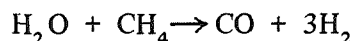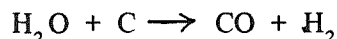
2. Hydrogenation of the oxygen-free aromatic compounds in the shale began as the temperature increased, resulting in distillates both of increasingly low H:C ratio (e.g. carbonite) and increasingly high H:C ratios (e.g. ozocerite).

3. Simultaneously, polymerization of the cyclic and olefinic constituents took place.

4. Organic molecules containing oxygen and nitrogen concentrated in the low boiling fraction of the series to form the elaterites and mutabilites.

5. The resulting organic fractions separated into immiscible liquids and solidified or plastified as they cooled.

Later, Mueller postulated that the melting points of these bitumens (which he considers to range from 85° to 310° C) indicate the temperature of the hydrothermal fluids at the time of their deposition, and that they can serve as a geological thermometer (Mueller, 1970).

Mueller's work is of limited usefulness because many of his field and laboratory observations are biased by his apparently strong desire to prove his genetical theories. Furthermore, much of his thinking ignores relatively well established scientific concepts in favor of his own. One example of the problems encountered in interpreting Mueller's work is his nomenclature system.

Mueller did not categorize the bitumens according to the previously established system (see Table III) but rather on the basis of O:C and H:C ratios. However, he makes no effort to determine whether any of the bitumens have been oxidized by ground water or air, even though there is strong evidence that secondary oxidation of the associated minerals has taken place. In addition, O:C ratios are a poor basis for a classification system because oxygen is determined only indirectly from combustion analysis and is subject to a larger error than are measurements for C, H, etc. Mueller's nomenclature is further complicated by the fact that he changed several of the original names in later publications. For instance Olefinite became Bernalite and Mutabilite, Foxite (presumably these are honorariums after J. D. Bernal and S. Fox, respectively).

Mueller's work is also diminished in value by the fact that his theory concerning the geologic history of these bitumens is based on numerous unsubstantiated observations and assumptions. For instance, he concludes that the temperature of the hydrothermal fluids reached as high as 310° C because one of the bitumens melts at this temperature. However, this particular bitumen appears to decompose rather than melt at this temperature. Also, studies of fluid inclusions from minerals in this area indicate that the temperature of the hydrothermal fluids rarely exceeded 120° C (Roedder, 1969). In another instance, Mueller invokes a fractionation process (phase 4 of his genetical history, page 37) which is contrary to the well known tendency for oxygen and nitrogen containing compounds to concentrate in the highest boiling fractions of petroleum because of their lower volatility, ease of poly-merization, and polarity (Ball, 1951). It is also extremely dubious that water would react

even at 300° C to form carbon monoxide and hydrogen from methane and carbon.

Thus, in spite of the fact that Mueller thinks it "outright impossible to visualize a(nother) process which would bring together in such a small space bitumens of such divergent primary properties be their origin sedimenary or magnetic (*sic;* perhaps he means "magmatic")" (Mueller, 1963), a renewed study of the deposit seems desirable to determine the fate of the sediment derived hydrocarbons.

The general approach in this study is to examine chemical and physical differences between the bitumens and the organic matter in their parent sediments, in the light of geologic evidence associating the bitumens with these sediments and with the mineralization process. Emphasis has been placed on the distribution patterns of the aliphatic alkanes and on the characteristics of the unfractionated organic matter, as determined by elemental analysis and infrared spectrophotometry. Parent sediments for the bitumens are identified by a combination of field geologic relationships and similarities in chemical composition among the various forms of organic matter. This approach is somewhat similar to that used in the correlation of bitumens with lithologically distinct source rocks in the Uinta Basin, Utah (Hunt, Stewart and Dickey, 1954).

Geologic Setting

The Bitumen Deposit

The bitumen deposit is located on Windy Knoll, in the northern part of County of Derbyshire, England (Fig. 9). This area lies about 160 miles north of London and 2 miles west of Castleton, the nearest village (Fig. 10). The deposit is easily reached by a two-minute walk from a paved, two-lane road. Treak Cliff Cavern, the source of most of the fluorite samples, lies one mile southeast of Windy Knoll along the same highway, and can be entered via a graded walkway provided for tourists.

The bitumens are in a deposit eight feet long and three feet high, near the top of the Windy Knoll promontory. The upper surface of the deposit is hidden beneath

Fig. 9.–Index and Geologic map of the Pennines Area. Adapted from Edwards and Trotter (1954).

N

MILES
0 50 100

LANCASHIRE
CHESHIRE

YORK

DERBY — NOTTINGHAM

LEICESTER

LONDON

ASKRIGG

INGLETON

IRISH SEA

YORK

PENNINE ANTICLINE

VALE OF YORK

SHEFFIELD

CASTLETON

HARDSTOFT

DERBYSHIRE DOME

EAKRING

N

MILES
0 15 30

NOTTINGHAM
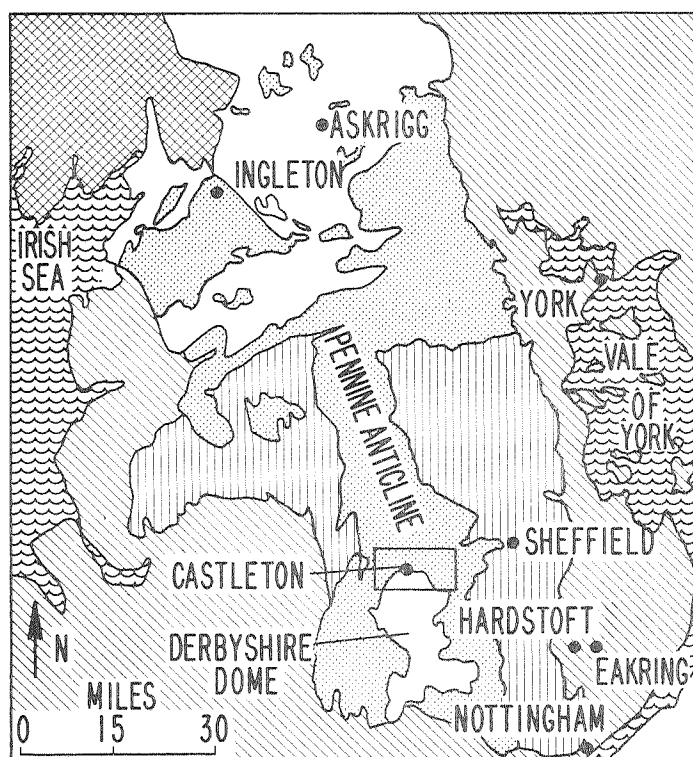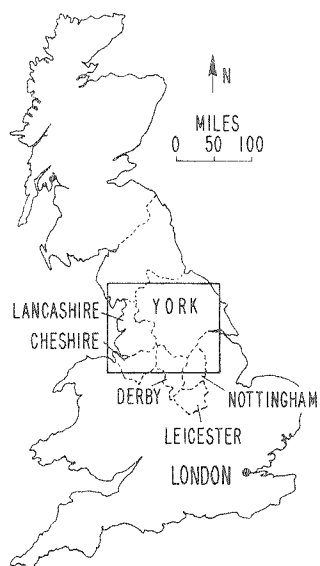
PERMO-TRIASSIC ROCKS

UPPER CARBONIFEROUS
COAL MEASURES

UPPER CARBONIFEROUS
MILLSTONE GRIT

LOWER CARBONIFEROUS
LIMESTONE

PRE-CARBONIFEROUS ROCKS

Fig. 10.–Geologic map of the Castleton area. Adapted from the Ordinance Survey of Great Britain map "Chapel En Le Frith Sheet No. 99."
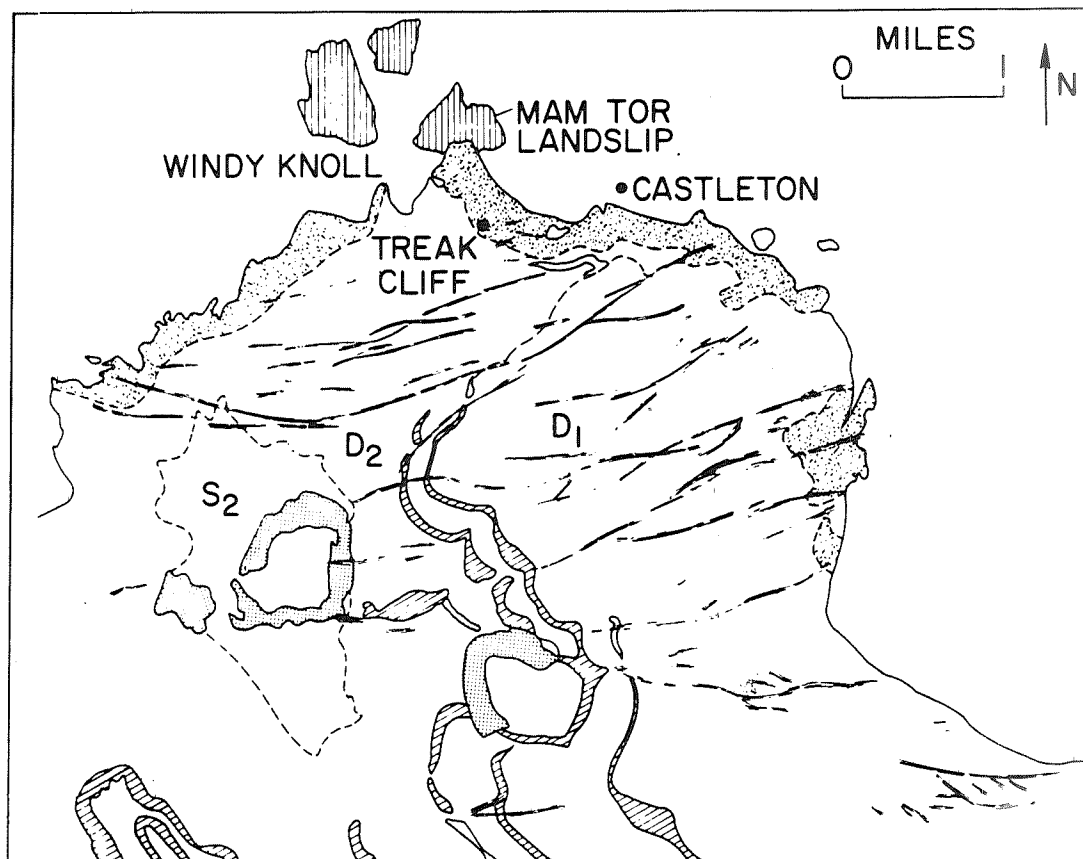
MILLSTONE GRIT

D_2 MONSAL DALE GROUP ⎫
D_1 BEE LOW GROUP ⎬ CARBONIFEROUS LIMESTONE SERIES
S_2 WOO DALE GROUP ⎭

LAVA

DOLERITE

LANDSLIP MASSES

REEF COMPLEXES

MINERAL VEINS

grass-covered soil, so that from a distance it appears as a dull, dark patch lying on the curved surface of a contrastingly light grey limestone (Fig. 11). At the time of this study, a vertical strip of the limestone was constantly wet from water running down its face. The exterior of the deposit is tough, rubbery and sticky. A solid, reddish brown material cakes the upper part and intermittently drops off during the warm season when the oil behind it softens and is pushed out toward the surface. Unweathered samples of the organic matter are best dug out with either a metal spatula or the wedge edge of a geologic hammer.

At least three types of organic material, distinguishable by their physical characteristics, are in the deposit. These tend to concentrate in layers roughly paralleling the limestone surface. The upper one foot consists of a greenish brown, gelatinous oil, which is locally called Elaterite (Fig. 12). It oozes out between angular fragments of limestone two to three inches in diameter. Scattered crystals of marcasite, galena, fluorite, etc., fine particulate matter, and interspersed drops of water are suspended in the oil. In places, the water content is high enough to give it the appearance of a viscous foam. Some of the water droplets are coated with a bright, red-brown solid, which is probably an iron oxide, and a white, opaque solid which is possibly anglesite or cerussite.

In the middle part of the deposit, this oil serves as a matrix for a conchoidally fracturing, brittle bitumen which closely resembles a dark, red-brown resin (Fig. 12 and Fig. 13). A freshly exposed surface of this bitumen is completely homogeneous in appearance, with no entrapped gas or liquid filled bubbles visible. The brown color becomes darker near the surface of the bitumen. The most striking form for this brittle bitumen is rods which are remarkably uniform in diameter (5-8 mm) and range up to five inches long. The same material is found as numerous spheres and globules ranging from microscopic to five millimeters in diameter. Some of the rods are thinned out and contorted, as if they were in a plastic state at the time of placement, and then hardened rapidly enough to "freeze" the flow structures. These rods are in pockets up to eight inches in diameter,

Fig. 11.–Photo of bitumen deposit at Windy Knoll (yellow strip in center of photo is two feet long). Below it is a sketch of details in the limestone hosting the deposit. Karst features are filled with limestone similar to surrounding rock and are not visible in the photo. The wavy lines near top of sketch approximate a fracture (?) pattern which seems to parallel the base of the bitumen deposit.
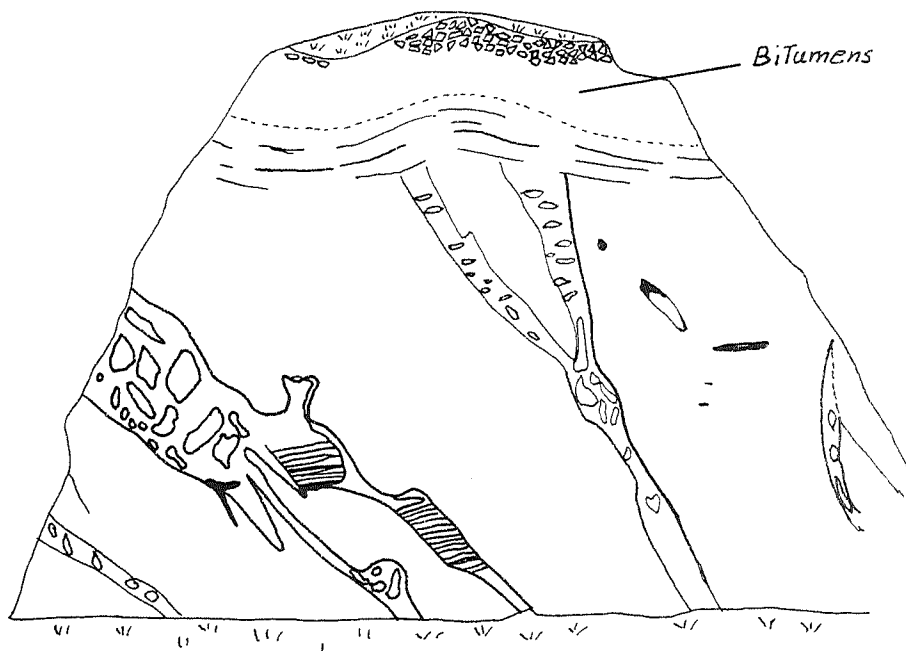
BiTumens

Fig. 12.--Photograph of the bitumen from Windy Knoll spread out on a glass plate to show particulate matter in the oil. A clear, brown bitumen globule, a cubic crystal of fluorite, and marcasite crystals are visible in the lower, right-hand part of the photo. Magnification X6 (Photo by Sally Craig)
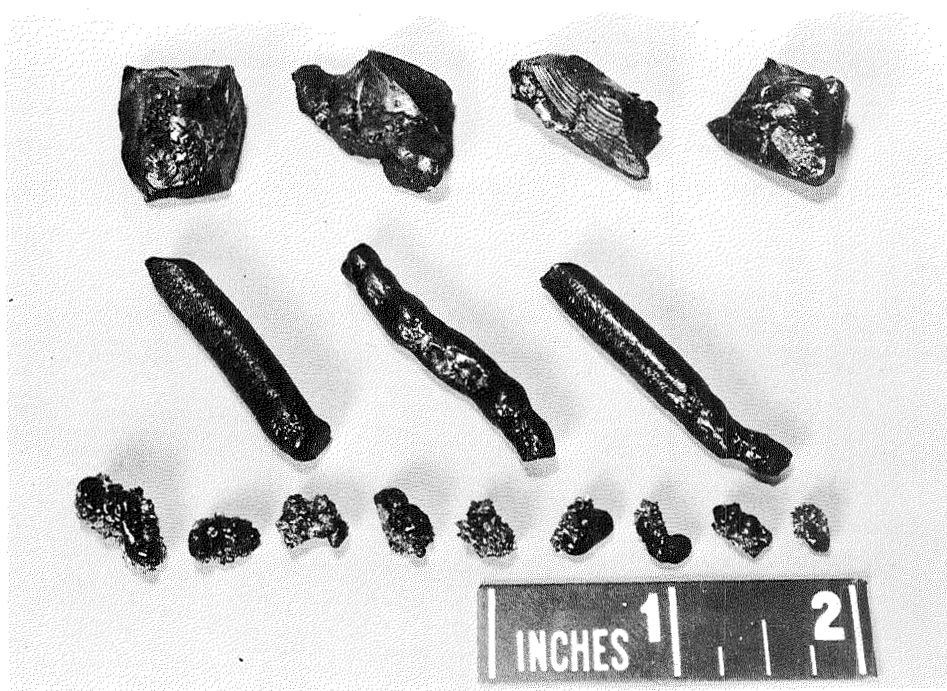
Fig. 13.--Photograph of the black bitumen from the main deposit (top row); and samples of the brown bitumen showing both the globule and rod shapes. (Photo by Ames Research Center)

the boundary of each pocket being defined by limestone fragments. Within a pocket, the rods are oriented parallel to each other and closely packed together, with only one or two millimeters of spacing between them. One pocket was found in which all the rods were disposed vertically, while six inches above it, another pocket was filled with rods extruding almost horizontally from the face of the deposit.

Conspicuously associated with the rods are marcasite crystals. These are usually found as clumps floating in the oil matrix around the rods. Remnants of a concave shell in many of the fragments indicate that they were once attached to the rods. Many of the rods still have massive aggregates of marcasite firmly attached to them (Fig. 14). These may be pulled off with effort to yield a shell whose inside surface mirrors the shape of the rods, and contains patches of the resin-like material. Examination of the crystals on the rods reveals that about 90% are oriented with their [101] face on top and their pinacoid face (usually unstriated) oriented nearly perpendicular to the bitumen surface (Fig. 15). That part of the crystal forming the exterior of the shell is euhedral, while at the interface with the bitumen, the crystals are subhedral to anhedral. Occluded among the marcasite crystals are rounded, subhedral crystals of purple fluorite about one-half millimeter in diameter. These amount to less than 1% of the volume of the marcasite.

Freely suspended in the oil at this level are crystals of purple fluorite (Fig. 12), calcite, galena, and quartz (see page 55 for details). Granular calcite containing many occluded mineral fragments and bitumens is also present.

A third form of bitumen predominates in the bottom layer of the deposit. It is a brittle, shiny black material which forms a discontinuous band about two inches thick along the lower boundary of the deposit, and also appears as large, chunky fragments up to three inches in diameter (Fig. 13). Massive calcite is associated with this black bitumen. Several pockets of calcite in the limestone within 100 ft of the main deposit also contain this black organic material dispersed as a fine powder along cleavage planes.
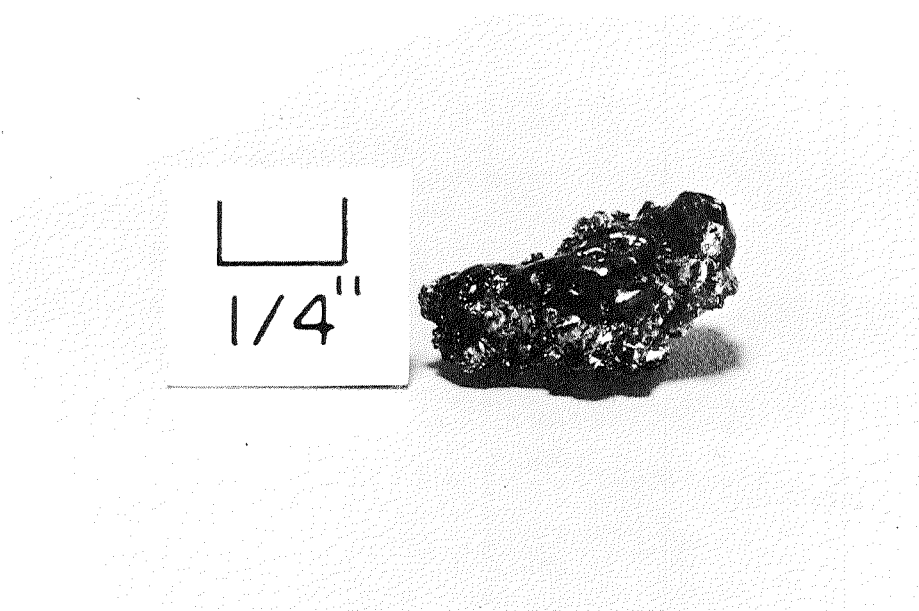
Fig. 14.–Photograph of one brown bitumen globule showing the massive aggregates of marcasite adhering to its surface (Photo by Ames Research Center)
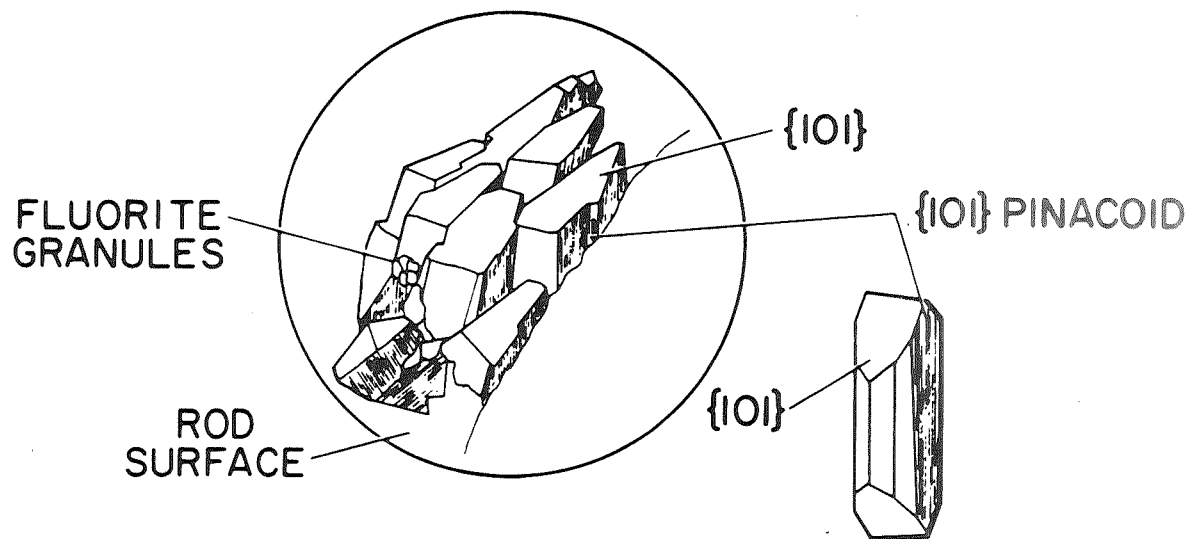
Fig. 15.--Sketch showing the orientation of the marcasite crystals on the surface of the brown bitumen. Magnification X6.

The limestone fragments in the bitumen deposit are composed almost entirely of granular calcite interspersed with a similar, black bitumen (Fig. 16). Random, small vacuoles filled with a hard, clear green, fluorescent hydrocarbon are exposed if these limestone fragments are broken. Small casts of fossils and recrystallized crinoid stems are also present.

Regional Geology

The origin and geochemical history of the organic matter at Windy Knoll is best developed by first considering it as one aspect of the geology of the Pennines region. The following summary of this geology is taken from papers covering the local geology and sedimentation of this region; a more detailed review is given in more detail by the Geological Survey of Great Britain (Edwards and Trotter, 1954).

The basement of the Pennine region is exposed as a group of Cambrian or Precambrian slates and sandstones in the Ingleton district (Fig. 9). Scattered outcrops of Ordovician shales and rare limestones, along with Silurian sandstones, shales, and flagstones appear in the northeastern part of the region. More than 80% of the Pennine rocks are of Carboniferous age. The Lower Carboniferous consists almost entirely of limestone, which reaches a maximum thickness of 5,000 ft in the northern Pennines and the Derbyshire hills. In the central Pennines, the Lower Carboniferous rocks are concealed beneath Upper Carboniferous rocks.

Aside from two groups of Upper Carboniferous limestones in the north Pennines, the Upper Carboniferous is composed of the lithologically distinct Millstone Grit Series. This consists of mudstones, shales, and sandstones which reach their maximum thickness of 6,000 ft near the Pennine uplift. The series extends south from west Yorkshire as a broad belt, paralleling the Pennine anticline, and narrowing down towards the Peak district, where Grit rocks almost surround the limestone hills of Derbyshire. Overlying these rocks are the Upper Carboniferous Coal Measures: a series of shale, sandstone, and

CLEAR, GREEN FLUORESCENT
HYDROCARBON FILLED VACUOLE

GRANULAR CALCITE AND BLACK
BITUMEN MATRIX

BRITTLE, BLACK SOLID
BITUMEN SEGREGATIONS

SHELL IMPRINT

RECRYSTALLIZED
CRINOID STEM
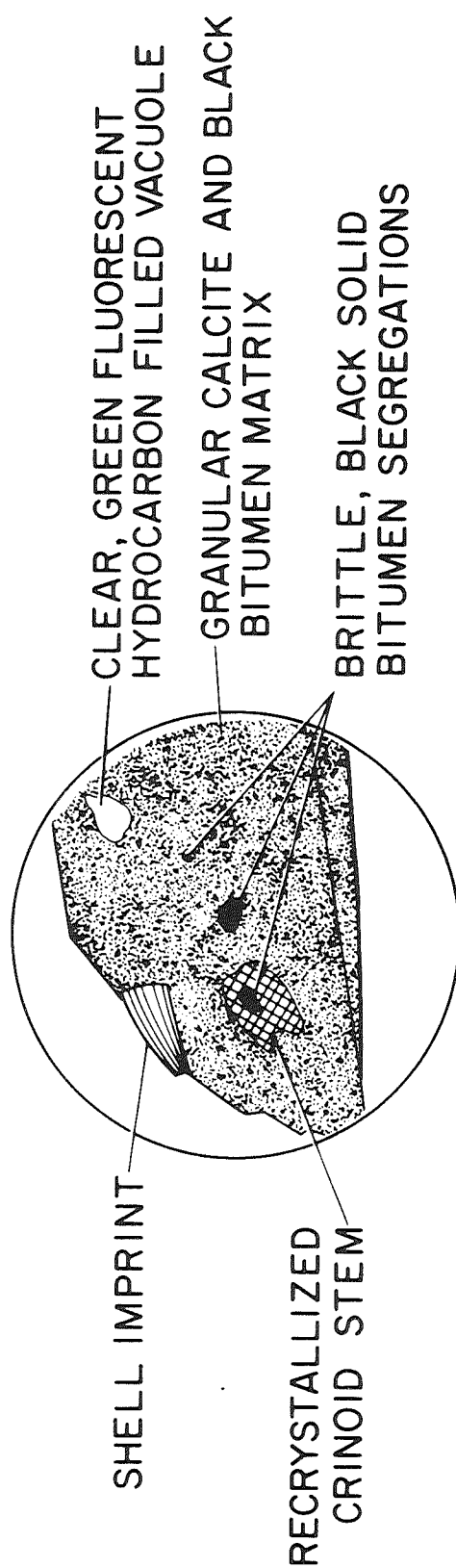
Fig. 16.--Sketch of a fresh surface of a limestone fragment in the Windy Knoll bitumen deposit. Magnification X6

coal cyclothems covering an area of 3,000 sq miles and reaching a thickness of 5,000 ft. These are best exposed as the coal fields of Lancashire and Cheshire on the western flanks of the Pennines, and of Yorkshire and the East Midlands to the east.

The only major oil field in Britain is at Eakring in a large anticlinal fold in the basal Coal Measures and the Millstone Grit on the eastern flank of the Pennine monocline. It is thought to have formed as oil migrated upwards from the underlying Grit shales and became trapped in porous horizons (Kent, 1966). Rare oil reservoirs in the Carboniferous Limestone, such as at Hardstoft, are considered to be the result of downward migration of oil from the lower Millstone Grit shales to porous limestone horizons near the unconformity (Kent, 1954). Indeed, almost all of the recorded oil showings associated with the limestone lie near the unconformable overlap of the Millstone Grit onto the limestone (Lovely, 1946).

Permian and Triassic sandstones and marls crop out in a continuous strip between Darlington and Nottingham. They also form the whole Cheshire plain and west Lancashire, where they are 5,000 ft thick.

The oldest Pennine rocks were laid down in a geosynclinal trough which extended from Europe to North America (Lovely, 1946). During the ensuing Caledonian orogeny, most of the British Isles was elevated into a land mass so that Devonian rocks are absent in this region. Deposition of the Lower Carboniferous rocks marked the transgression of Devonian European seas across Britain and the beginning of the Carboniferous geosyncline of central Europe. This period was followed by a silting up of the sea and concomitant, mild tectonic deformation of the rocks, producing the fresh water and deltaic rocks of the Upper Carboniferous period. Permian and Triassic deposits were laid down in the western part of the saline Zechstein sea of Germany, which regressed eastwards during Jurassic times. Erosion during Tertiary time formed the broad features of the present Pennine Hills.

The most important deformations in the Pennine region took place during the Hercynian orogeny, which began during Carboniferous times and culminated in the late Carboniferous or Permian. During this orogeny, NNW-trending anticlinal uplifts and the north-south fold line, the Pennine Anticline, were generated. Toward the south, a number of folds developed providing trough-like synclines which are now the productive coal fields. The anticlines of Hardstoft (Derbyshire) and Eakring (Nottingham) were among these. Post-Triassic, possibly Tertiary, movements caused domal elevation of structural units in the west and elevation of the north-south trending Pennine axis. The massifs of the Askrigg Block and the Derbyshire Dome are in part structurally defined features developed during the Hercynian orogeny. Doming of the blocks during Permian times may have resulted in the formation of the ENE, NNW, and WNW fracture patterns in which ore minerals are now deposited (Fig. 2).

Hydrothermal Mineralization

Hydrothermal mineralization in the Pennines has been described by Dunham (1968) and Sawkins (1966), and details of the mineralization in North Derbyshire by Ford (1955, 1964, and 1969).

The Castleton area is in the northernmost part of the Derbyshire lead-zinc orefield. The distribution of orebodies here is controlled by fractures in the limestone, such as at Odin Rake, with the overlying Edale Shale acting as a cap rock for the fluids. Fluorite deposits in the limestone along the Treak Cliff scarp are not particularly associated with the fractures but rather with the boulder bed along the limestone-shale unconformity, where massive, radiating layers of the purple and white mineral fill voids between the boulder-bed blocks (Fig. 17). Metasomatic replacement of the limestone by fluorite is evidenced by massive fluorite containing recrystallized crinoid stems, and euhedral, cubic crystals of fluorite dispersed in otherwise unaltered limestone. The purple form
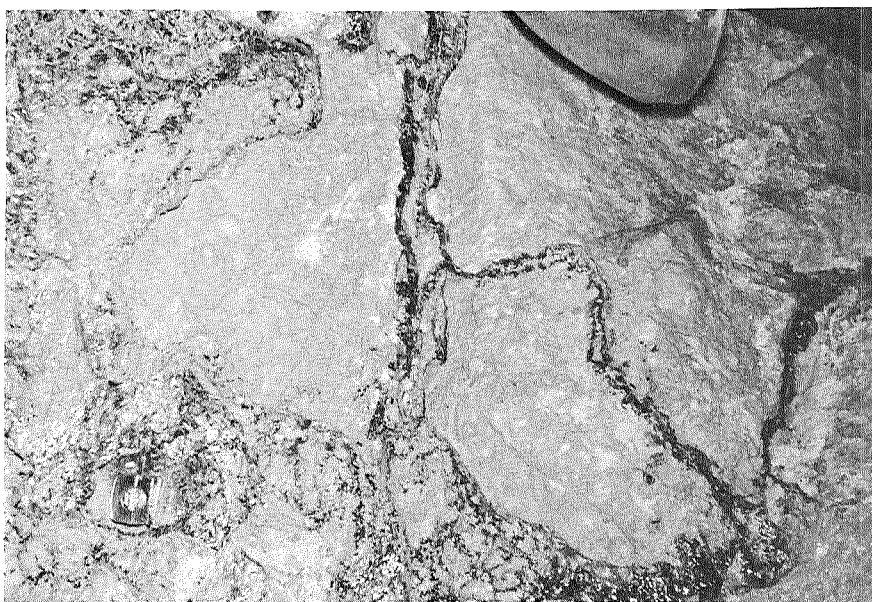
Fig. 17.--Fluorite between limestone blocks of the boulder bed in Treak Cliff Cavern (Photo by K. L. Pering)

of fluorite is usually associated with mineralized areas contacting the Edale Shale. This association has suggested to some people that the color is due to organic matter from the shale which was incorporated into the fluorite (Ford, 1955). That heating of this fluorite yields some volatile organic matter, was shown in 1920 (Garnett), and Mueller (1952) speculates that a form of bitumen in the deposit at Windy Knoll is also in the fluorite and gives it its purple color.

The sulfide minerals present in the orefield are: galena (the major ore mineral), sphalerite, chalcopyrite, pyrite, and marcasite. Fluorite, with minor quantities of barite, calcite, quartz, and dolomite constitute the non-sulfide minerals. At Windy Knoll, euhedral, cubic crystals of fluorite; rhombohedral calcite; euhedral, octahedral galena; and subhedral crystals of quartz are suspended within the bitumen deposit, but the limestone host rock is not mineralized. About twenty feet west of the deposit, massive, milky white, crystalline calcite appears in the limestone. Almost buried beneath the soil, fifteen feet to the north, there are pockets of tiny, cubic crystals of purple fluorite in the limestone dispersed with calcite and bitumen (Fig. 18 and Fig. 19). A consistent paragenetic sequence for these minerals is not clear. However, since the largest deposit of lead in the Windy Knoll area is at Odin Rake, and the fluorite is localized around it, along the limestone scarp, the rake appears to be one of the main local sources of the fluoride-bearing solutions. Over the whole orefield, there is an increase in fluorite in an easterly direction, followed by barite, and an increase in calcite in a westerly direction.

Fluid inclusions in fluorite from North Derbyshire place the temperature of deposition at about 80° C (Roedder, 1969), while late primary and pseudo-secondary inclusions indicate a possible second phase of mineralization at about 140° C. Little geochemical work has been done in the North Derbyshire orefield, but in the Northern Pennine orefields, high potassium concentrations in the fluids (from the inclusions) suggest that the ore-bearing solutions rose from deep parts of the earth's crust. Mineral formation in the rising fluids
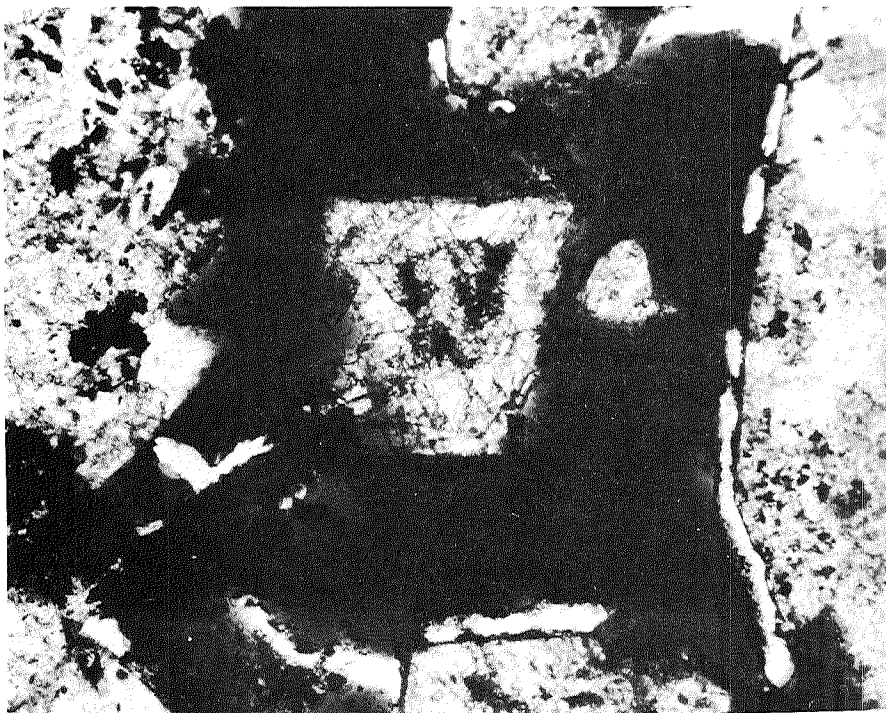
Fig. 18.--Brittle, brown bitumen surrounding a fluorite crystal in a massive fluorite-calcite-bitumen aggregate
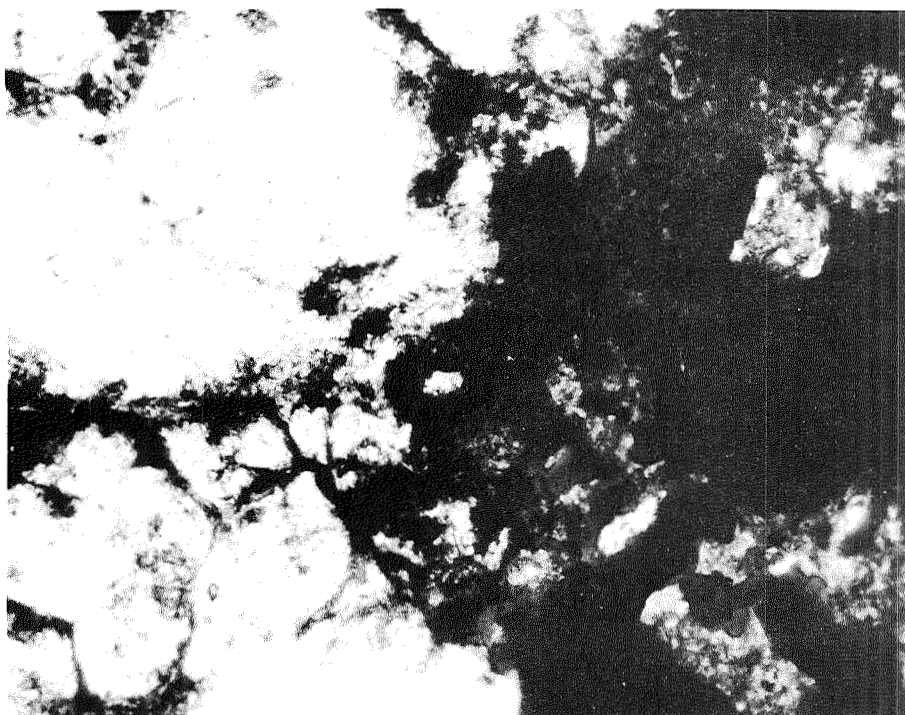
Fig. 19.--Massive fluorite-calcite-bitumen aggregate showing brown material similar to that in Fig. 22, page 65, in addition to the clear brown bitumen

appears to be largely controlled by the temperature of the cooling fluids, although mixing of the fluids with connate brines may have introduced barium, causing precipitation of barite. The time of mineralization in the Derbyshire orefield is placed at late Triassic on the basis of mineralization of basal Triassic sands and gravels in the southern part of the ore field. Model lead ages in the range of 180 ± 40 my are also in this range (Moorbath, 1961).

North Derbyshire Geology

Details of the geology of the Castleton area have been published by Ford (1955), Simpson and Broadhurst (1969), Parkinson (1953 and 1956), and Shirley and Horsfield (1940). The limestone which composes the Derbyshire dome is relatively uniform compared with adjacent rocks, and stands at a higher elevation. Hence, it is often referred to as a massif. It is fringed on the north and east by a remnant band of reef limestone with a fore reef slope which forms a prominent scarp 400 ft high near Castleton marking the original surface of the reef front (Fig. 10). Windy Knoll is a rounded and topographically prominent knoll of this reef limestone, forming a structural high near the top of the massif at its extreme northern edge (Fig. 20). The erosional surface of the limestone dome is covered by remnants of a boulder bed at Windy Knoll and Treak Cliff which formed before deposition of the Edale Shale. It is composed of large limestone blocks with a broad lithological range; the blocks range in size up to several yards in diameter, and are associated with smaller blocks, pebbles, and fossil fragments. Extensive cave development at Treak Cliff and Blue John expose the boulder bed and karst features in the underlying massif limestone. Surrounding the massif is the basal Edale Shale of the Millstone Grit series. This rock crops out within 200 ft of Windy Knoll, where it is exposed by the Mam Tor landslip. The only igneous rock in the area is the basaltic lava exposed in Cave Dale. Further south, around Peak Dale, intrusive sheets and necks of dolerite, known locally as toadstones, and interbedded basalt and tuff are exposed in the limestone.

Fig. 20.--Cross section through Windy Knoll showing relationships between the lead and fluorite deposits, the boulder bed, and the bitumen deposit on Windy Knoll

WINDY KNOLL (1375')   SHALE

BLUE JOHN
MINE

ODIN
RAKE

CROSS SECTION THROUGH WINDY
KNOLL ALONG TRAVERSE A' A
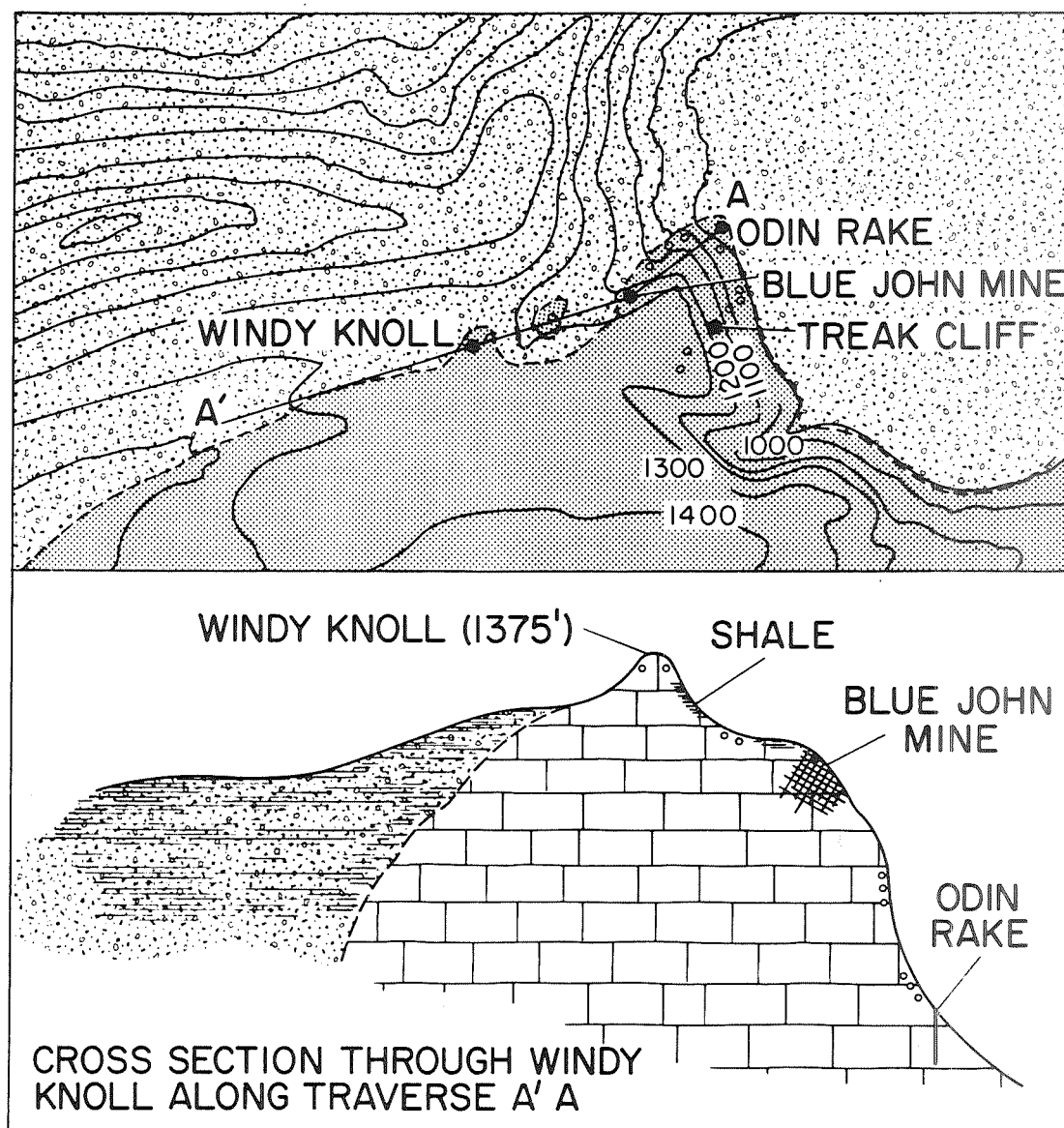
VERTICAL SCALE 3 TIMES HORIZONTAL
11cm = 3000' HORIZONTAL

∘∘∘   BOULDER BED OUTCROPS
      (SIMPSON & BROADHURST)

▨   MASSIVE PURPLE FLUORITE

▤   EDALE SHALE

▥   LIMESTONE

——   ORE FILLED FISSURE

The limestone of the dome is a clear-water facies rock. It is best exposed in Winnats Pass as a massively bedded, aphanitic, grey limestone. On the plateau above Castleton, crinoid debris is profuse. In the Castleton area, the limestone is of Visean Age on the basis of coral-brachiopod zones D_2 and D_1, and the Goniatite subzones P_1, B_2, and B_1 (Wolfenden, 1955).

The porosity of the limestone matrix is almost zero. Most of the visible porosity is secondary, as open joints and fissures (now, or at one time filled with ore) and hollow chambers in shell fragments which are usually lined with a thin layer of drusy calcite. Little porosity can be associated with the karst features, as the detritus in these is cemented with a calcite matrix. The absence of significant oil in the Lower Carboniferous limestone is attributed to a very limited mobility of the organic matter within this non-porous carbonate matrix. Microscopic examination of the rock shows that segregated organic matter in the limestone is predominantly black particulate matter which con-centrates along boundaries between recrystallized and unrecrystallized calcite grains (Fig. 21 and Fig. 22). Macroscopic occurrences of organic matter have been reported in this area (Mueller, 1954a), but most of these occurrences are no longer accessible. The most common type is the dark yellow, viscous oil called Elaterite (apparently the same as that of the same name at Windy Knoll). A second form is a black, shiny solid material associated with calcite veins and fossil cavities in the limestone.

The reef complexes cropping out at Windy Knoll, Castleton, and Winnats Pass are considered to be calcareous algal reefs with Stromatolite structures. Like the dome lime-stone, the reef rock is a pale grey, aphanitic limestone, but has very few crinoid fossils. Its porosity is also limited to secondary fractures and cavities. The limestone blocks in the boulder bed are derived from higher parts of the dome and are thus lithologically the same as the massif and reef limestone. The matrix of the boulders ranges from a soft calcareous mud, such as at Treak Cliff (Fig. 23), to a highly indurated, calcareous cement, as at Windy Knoll (Fig. 11).
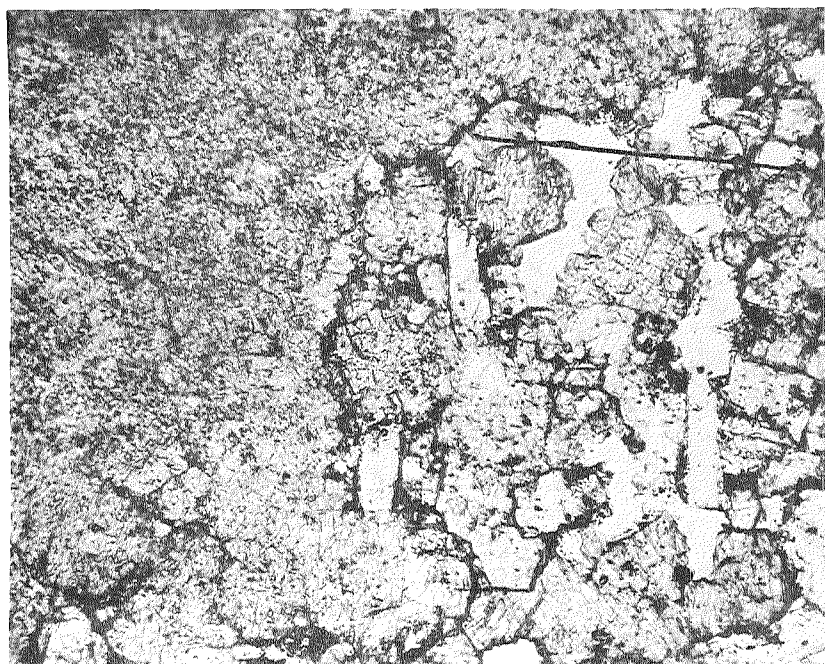
Fig. 21.–Black, opaque material (clay-organic?) concentrated in bands adjacent to recrystallized parts of the limestone. Sample from Treak Cliff Cavern; Magnification X140 (Photo by Sally Craig)
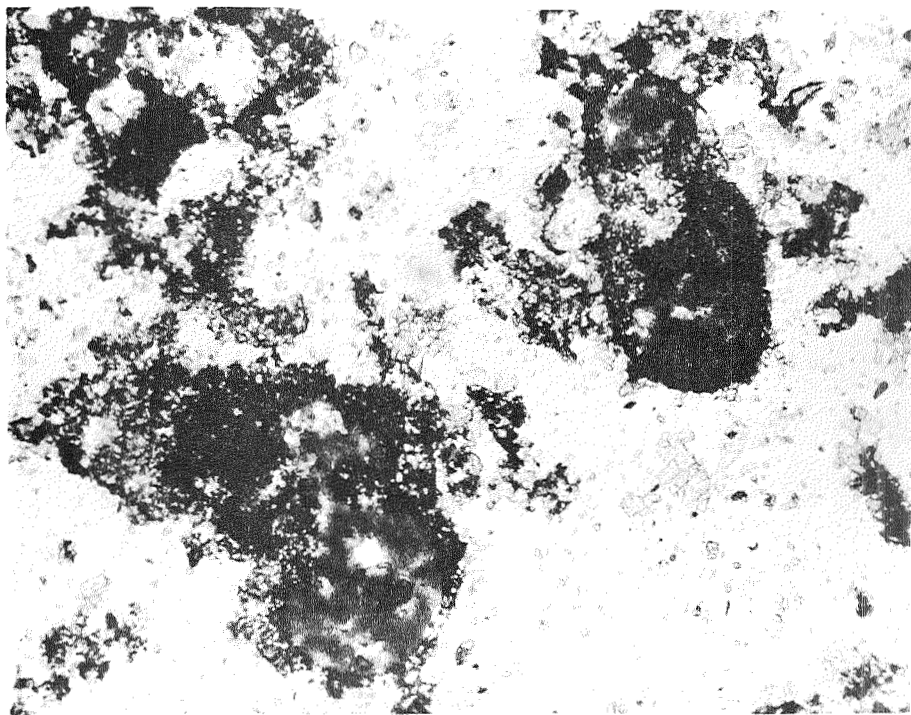
Fig. 22.--Black, opaque material in unrecrystallized limestone from Windy Knoll quarry. Magnification X140 (Photo by Sally Craig)
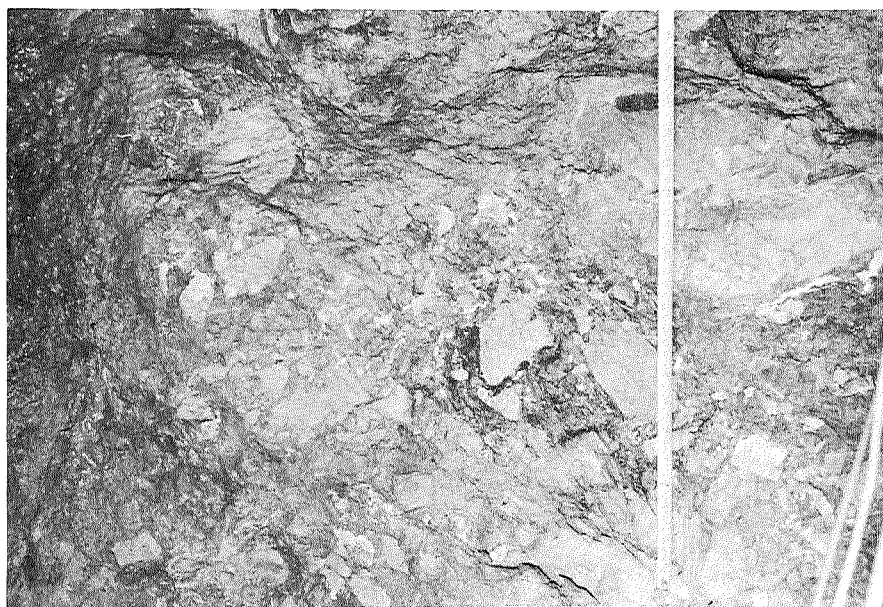
Fig. 23.--Boulder bed exposed in Treak Cliff Cavern, showing dark, clay matrix (Photo by K. L. Pering)

The Edale Shale is best seen at the base of Mam Tor as a dark brown, calcareous mudstone containing a one foot thick band of silty limestone. Here, the thinly laminated mudstone shows impressions of pelecypods, but goniatites, which are a common fossil in the shale, were not seen. Opposite Mam Tor, the shale in the landslip masses is highly fissile. The partings show no fossils, and the plates are coated with a glossy surface which may be organic, or iron stain. In the same shale are scattered pyrite nodules about five millimeters long. The shale partings in most of these areas are coated with a sludge of clay and free sulfur. The freshest exposures of this rock are presently at the Raper Mine, about 12 miles south of Castleton (Fig. 24). The Edale Shale is quite rich in organic matter, as indicated by the fact that hollows in goniatite fossils have been found filled with a dark brown oil (Edwards and Trotter, 1954).

The North Derbyshire Massif represents a tectonically stable region of deposition during the latter part of the Lower Carboniferous. The reef limestone along the edge of the massif marks the margin of the sedimentary basin on the north and east sides of this region. Uplift of the region in mid-Carboniferous times permitted subaerial erosion of the limestone surface, producing karst features and leaving blocks, boulders, and gravelly limestone along its surface. In late Carboniferous times, subsidence resulted in deposition of the Edale shales over this surface. Later action of ground water enlarged fissures in the solid limestone beneath the shale and created the caves during Tertiary or Pleistocene times of Treak Cliff and Blue John. Mild tectonic deformation during the Hercynian orogeny began folding the basin area, and fractured the limestone along Odin Rake. Presumably, mineralization in the Castleton area began as hot fluids welling up along this fissure deposited lead ore in the fissure and migrated through solution cavities and pores of the boulder bed, up the steep limestone scarp formed by the front of the reef. (For a detailed description of the complex sequence of mineralization events see Ford, 1967). The cooling fluids deposited fluorite both directly and by replacing the limestone along the unconformity. Mixing with

Fig. 24.--The open pit Raper Mine exposing the Edale Shale in fault contact with mineralized Lower Carboniferous Limestone (Photo by K. L. Pering)

brines from the overlying shales may have hastened the cooling process, and contributed to the formation of the purple-colored fluorite. The unique concentration of bitumen at Windy Knoll may be the result of entrappment of the fluids under hydrodynamic conditions (Hubbert, 1953) as they migrated along the unconformity.

Experimental

Infrared spectra were run as liquid films (Perkin Elmer 521) unless otherwise stated. Gas chromatographic conditions are given in the figure legends. Elemental compositions were obtained from duplicate combustion analysis.

Edale Shale

Three samples of shale from about the same stratigraphic horizon were analyzed: Sample I-S is from a recent road cut just below Treak Cliff Cavern, Sample II-S is from 200 ft NE of Windy Knoll at the base of Mam Tor, and Sample III-S is from the head of Odin Rake. Sample IV-S is from the Raper Mine and may not represent the same conditions of deposition as the others.

The shale was washed in water, then scrubbed with a clean bottle brush to remove as much as possible of the soft, muddy coating. The scrubbed plates were rinsed in distilled water and dried. The rock plates, ranging in size from three to six centimeters in diameter and one half to one centimeter in thickness were broken up in a mortar to about two centimeter chunks. These were refluxed again in benzene for several hours. The cleaned pieces were then ground in a stainless steel ring crusher until the material passed through a 200-mesh sieve. A 250 g sample was sonicated three times for 10 min in 300 ml benzene-methanol (9:1).

Evaporation of the extract from Sample II-S yielded 654.1 mg of a dark, brown-green viscous oil. An infrared spectrum was recorded and whatever material would dissolve in benzene was chromatographed on 50 g alumina with hexane to obtain the aliphatic

hydrocarbon fraction. The hexane eluant was usually a pale yellow color, indicating the presence of free sulfur. This was removed by passing the hexane over a column of colloidal copper three centimeters long (Blumer, 1957). The purified aliphatic fraction for Sample II-S weighed 75.5 mg. The weight of the fractions from the remaining two samples was not obtained because evaporation results in loss of some of the more volatile components.

The branched-cyclic fraction of the aliphatic hydrocarbons isolated from the Raper Mine shale was separated from the straight-chain isomers by molecular sieving. Granular, 5 A° Linde molecular sieve (30/60 mesh, Wilkens Instrument Co.) was dried for 12 hrs at 350° C and stored in a desiccator. About 50 mg of the alkanes were added to 50 ml dry benzene and placed in a 100 ml round-bottomed flask. About two grams molecular sieve was added and the mixture refluxed for eight hours. The benzene was decanted off and evaporated to obtain the branched-cyclic fraction.

Lower Carboniferous Limestone

Two of the limestone samples analyzed were collected from inside Treak Cliff Cavern. Sample I-L is an aphanitic, light-grey, fossiliferous rock with uneven patches of dark, homogeneous limestone dispersed in it. Collected on the upper right-hand part of the cavern, this rock is probably part of the boulder bed. Sample II-L is an aphanitic, grey limestone from a small cave to the left of the main cavern. There is no evidence of a boulder bed matrix here, and this rock is probably part of the fissured, massif limestone. a third, Sample III-L, is a pale grey rock collected from the face of Windy Knoll quarry, about 10 ft north of the bitumen deposit. This rock is probably a reef limestone, although it may be part of the boulder bed.

Sample II-L was analyzed by two different methods to determine which was the more efficient. The first method is dissolution of the carbonate matrix with hydrochloric acid and extraction of the saline solution with organic solvent. The second is direct

extraction of the ground rock with benzene-methanol (9:1). A detailed procedure is given with respect to this rock: the remaining samples were analyzed by the extraction method, which proved more efficient.

Sample II-L was cleaned by placing the pieces, about 4 x 4 inches in diameter, in a stainless steel beaker and covering them with 1N HCl. As evolution of CO_2 ceased, a few milliliters of concentrated HCl was added. After two to three hours, the acid cleaned rocks were rinsed in water and dried. The pieces were refluxed in benzene, dried, broken into halves with a hammer, and crushed in a jaw crusher. These fragments were then ground in a stainless steel ring crusher to about 200 mesh.

About 300 mls distilled water was added to 189 g of the powdered limestone. To this slurry, 6N HCl was added until 95% of the limestone had dissolved. The resultant black solution was divided into two 500-ml portions and each was extracted with three 300-ml portions of hexane. Benzene was not used because of its tendency to form emulsions. The extract was dried over $CaCl_2$ and evaporated to dryness. The residue was a white solid at room temperature and weighed 20.6 mg.

For the second method, 294.2 g of the powdered limestone was refluxed three times with 300 ml benzene-methanol (9:1). The extract was opaque and grey in color. To remove the colloidal material, it was evaporated just to dryness and the residue slurried with hexane. The colloidal hexane suspension was shaken in a separatory funnel with dilute HCl for about 10 min to dissolve the fine carbonate particles and clear the hexane. The clarified extract was dried over $CaCl_2$ and evaporated to dryness under nitrogen. The residue, weighing 61.7 mg, was dissolved in hexane and eluted off 20 g of alumina to yield a 65 mg aliphatic hydrocarbon fraction (the discrepancy in weights may be due to incomplete evaporation, or silica gel particles in the flask). The aliphatic hydrocarbons were chromatographed to obtain their distribution patterns.

Fluorite

The fluid inclusions in the Castleton fluorite are too small to permit isolation of the contents of an individual inclusion for study: thus, the probability of obtaining organic matter from only primary inclusions is small. The fluorite samples were analyzed using successively more rigorous crushing and cleaning procedures on the assumption that crushing would preferentially fracture the mineral along octahedral cleavage planes. Presumably, secondary inclusions forming along this set of planes would be removed in greater amounts than the contents of primary inclusions which tend to concentrate along the cubic faces of the crystal (Roedder, 1967).

A six by five inch sample of dark purple fluorite from Treak Cliff Cavern was rinsed in distilled water and then methanol and dried. The sample was broken into two-inch fragments and refluxed three times with benzene-methanol (9:1) overnight. The fragments were removed, crushed in a mortar, and then in a stainless steel ring crusher to pass through a 200-mesh screen. The powder (500 g) was sonicated with 400 ml benzene-methanol (9:1) for ten minutes three times. Evaporation of the solvent and chromatography on alumina yielded about one milligram hydrocarbons. Sample II-F was treated in a like manner except that the two-inch pieces were sonicated with benezene-methanol (9:1) for ten minutes, and then broken into one-centimeter fragments and sonicated twice before crushing to 200 mesh. A third sample (III-F) was crushed to one millimeter size and sonicated twice before finally crushing to 200 mesh. Two samples of white fluorite (IV-F, and V-F) were analyzed in the same manner as Sample II-F. The quantity of aliphatic hydrocarbons above nC_{12} isolated from these two samples is estimated from gas chromatography as about 0.1 mg per 500 g rock.

Hardstoft, Eakring and Plungar Crude Oils

Petroleum samples from the Hardstoft, Eakring and Plungar oil fields were obtained

from the British Petroleum Company. The first two are dark brown, medium weight oils and the latter is a heavy black crude. None of these oils have been affected by hydrothermal solutions, although the Plungar field may have been affected by an igneous intrusion (Falcon and Kent, 1960). Infrared spectra of the oils were recorded, and then about 0.5 ml of the oil was chromatographed on 50 g alumina.

Brown Bitumen

Representative samples of the brown bitumen were isolated with tweezers from the oil matrix material dug up from the center of the Windy Knoll deposit. The solid brown fragments were refluxed in benzene and air dried. Three hydrocarbon analyses were carried out on various specimens, but confirmatory mass spectrometry and destructive distillation were carried out on only one sample. Efforts to dissolve the bitumen in pyridine, dioxane, carbon disulfide, and chloroform failed. The bitumen is stable in sodium hydroxide at $100°$ C, but turns black when heated with hydrochloric acid at this temperature overnight.

For the first analysis, about 25 g of the rod-shaped bitumen were crushed in a mortar to a fine powder. The powder, weighing 21.44 g, was scraped into a soxhlet extractor and refluxed with benzene-methanol (9:1), for 12 hrs. The extract was evaporated almost to dryness under nitrogen to give a residue weighing 768 mg. An infrared spectrum of the extract was recorded and the material then chromatographed on 30 g of alumina. A portion of the aliphatic hydrocarbons was reserved for gas chromatography, and the remainder was refluxed with twenty times its weight of molecular sieve for 12 hrs to separate the straight-chain alkanes from the branched-cyclic isomers. The presence of isoprenoids was confirmed by collecting peaks corresponding to the retention times of the C_{18}, C_{19}, and C_{13} isoprenoids and reinjecting them onto a 12-ft polyphenyl ether column. Peaks corresponding to isoprenoids on this column were collected and vaporized into the direct probe of a CEC 103 mass spectrometer.

To elucidate the nature its infrared spectrum of a portion of the insoluble material remaining after extraction was recorded in a KBr pellet: the remainder was placed in an all-glass, bantamware, vacuum distillation system. The bitumen was heated to 165° C under house vacuum for two hours, cooled, and then washed with benzene-methanol (9:1). After drying, it was reheated to 260° C over a period of three hours, cooled, and washed again. The remaining material was finally heated to 310° C, cooled, and extracted. The aliphatic hydrocarbons in all three extracts were isolated by chromatography on silica gel after their infrared spectra were recorded.

Elaterite Oil

Samples of the viscous oil completely free from other bitumens were impossible to collect at Windy Knoll. Oil containing the least amount of particulate matter was extracted with benzene-methanol (9:1). The brown, fluorescent green extract was evaporated to dryness under nitrogen to yield a gummy, viscous residue. Three samples of this oil were examined. An infrared spectrum was recorded and the oil chromatographed on alumina. The aliphatic hydrocarbons were purified on silica-gel thin layer plates before gas chromatography. One sample was chromatographed, along with standards, on silver nitrate impregnated silica gel thin layer plates. A broad, unresolved band formed, indicating that unsaturated hydrocarbons were present. This band was scraped off, eluted, and the infrared spectrum of the eluted material recorded.

Black Bitumen

The three samples of black bitumen analyzed include two from the thick band along the bottom of the main Windy Knoll deposit, and one from a pocket in the limestone about six feet below this. The first two samples are hard, brittle material which is denser than water, and fractures irregularly (not conchoidally). The third sample has a much duller luster and crumbles easily to a fine powder (the first two will also, if sonicated). All three yield

about the same of organic material upon extraction: one of the first two bitumens, weighing 16.87 g, was sonicated in benzene-methanol (9:1) for 10 min three times. Centrifugation and evaporation of the solvent yielded 870 mg black asphaltic oil. An infrared spectrum was recorded and the oil chromatographed on alumina to yield 522.3 mg aliphatic hydrocarbons.

Results

Edale Shale

The infrared spectrum of the organic matter extracted from the Edale Shale indicates that it is composed primarily of aromatic compounds containing some oxygen and possibly sulfur (Fig. 25 (1)). Approximately 10% of this extractable material is aliphatic hydro-carbons which consist of an homologous series of straight-chain isomers and lesser amounts of branched-cyclic isomers (Fig. 26). These hydrocarbons form a distribution pattern which consistently maximizes in the nC_{15} region. The aliphatic hydrocarbons isolated from the Raper Mine Edale Shale show a smaller proportion of straight-chain isomers, so that the straight-chain and branched-cyclic components are in about equal amounts. Removal of the straight-chain isomers leaves a complex mixture of hydrocarbons in which the lower molecular-weight isoprenoid isomers are the prominent components (Fig. 27).

Lower Carboniferous Limestone

In contrast to the Edale Shale, infrared absorption of the extractable material from the Lower Carboniferous Limestone indicates a composition dominated by high molecular weight, paraffinic hydrocarbons, a moderate amount of which are oxygenated (Fig. 28 (2)). Aliphatic hydrocarbons make up more than 90% of this extractable material. The distribution of the hydrocarbons obtained by either method of extraction exhibited the same distribution patterns, characterized by a strong dominance of the high molecular weight, straight-chain isomers, which reach a maximum peak intensity around $nC_{21}-nC_{27}$ (Fig. 29).

Fig. 25.–Infrared spectra of bitumens genetically related to the Millstone Grit rocks

WAVELENGTH, microns

5   6   7   8   9   10   12 14

1 BENZENE METHANOL EXTRACT OF
  THE EDALE SHALE

2 BENZENE METHANOL SOLUBLE,
  PRODUCE FRACTION, LOW TEMPERATURE
  PYROLYSIS OF BROWN BITUMEN

3. BROWN BITUMEN, AS KBr PELLET

4. BENZENE METHANOL EXTRACT OF
   THE BROWN BITUMEN

5. HARDSTOFT AND EAKRING CRUDE OILS

6 PLUNGAR CRUDE OILS

2000   1500   1000   700
            FREQUENCY, (cm⁻¹)
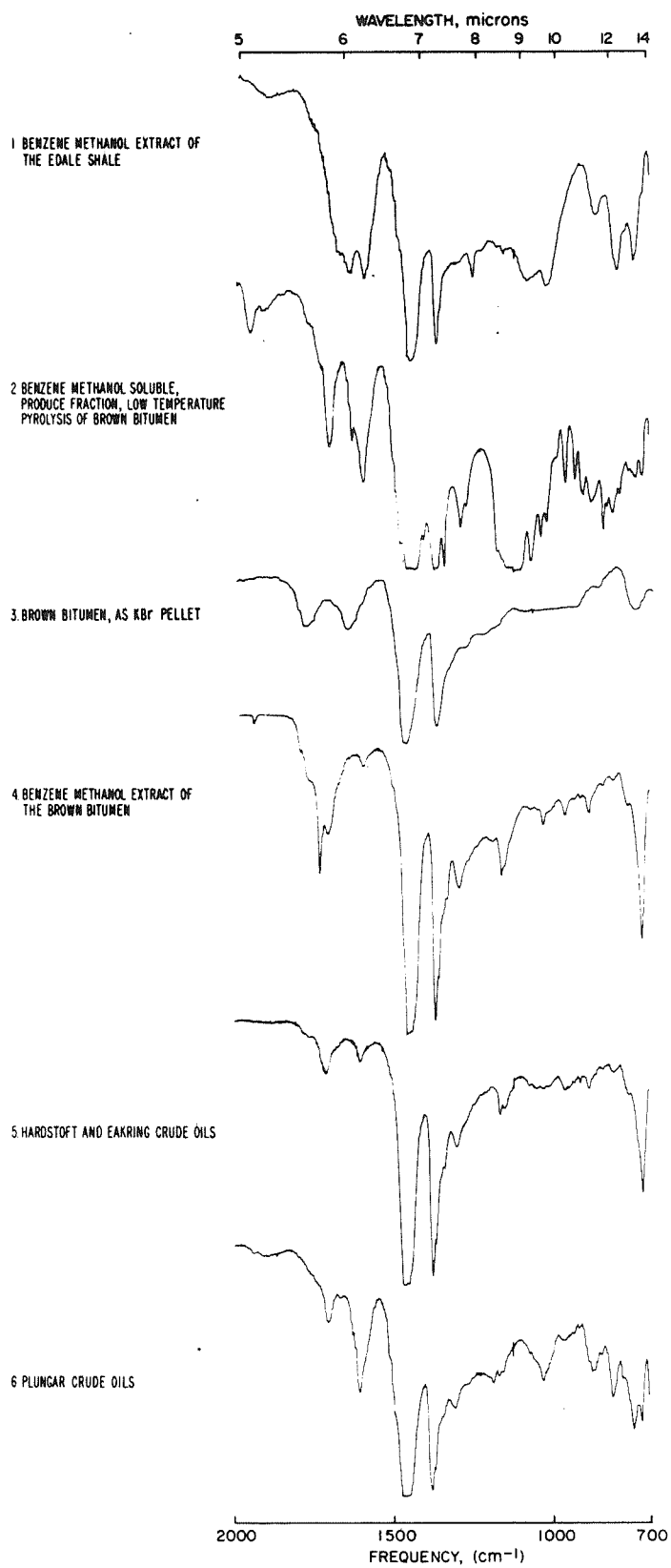
Fig. 26.--Aliphatic hydrocarbons extracted from the Castleton Edale shale; (a, b) Perkin Elmer 880; 50' OV-1 S. C. O. T. column; He flow rate 3 ml/min. Temp. prog. 2°/min; (c) Aerograph 660, 50' SE-30 F&M HiPak column; He flow rate 2 ml/min.; Temp. prog. 2°/min.

    (a) Sample II-s Att. X200: 200 ft from Windy Knoll

    (b) Sample I-S Att. X50: Below Treak Cliff

    (c) Sample III-S Att. X50: Just above Odin Rake

(a)

(b)

(c)

TEMPERATURE, °C
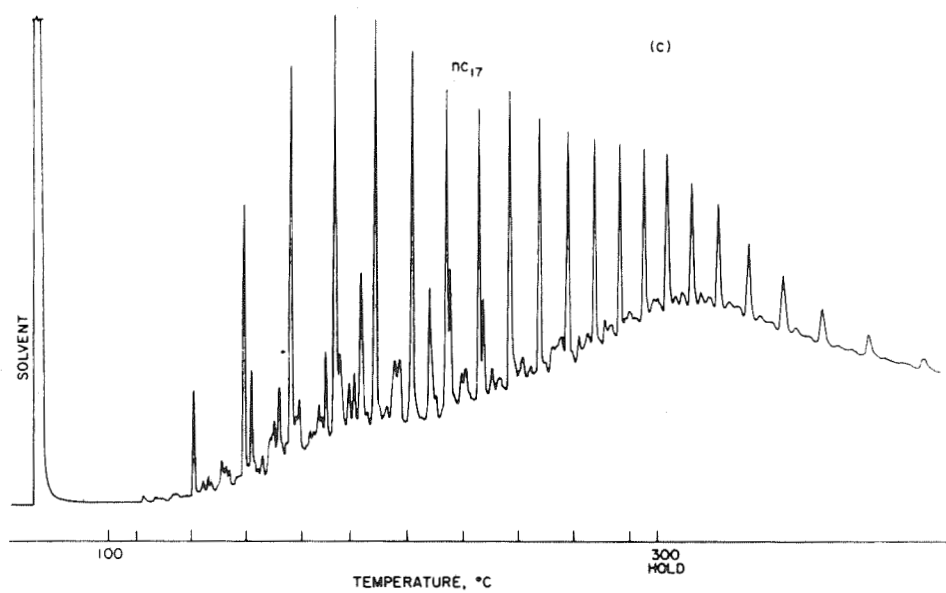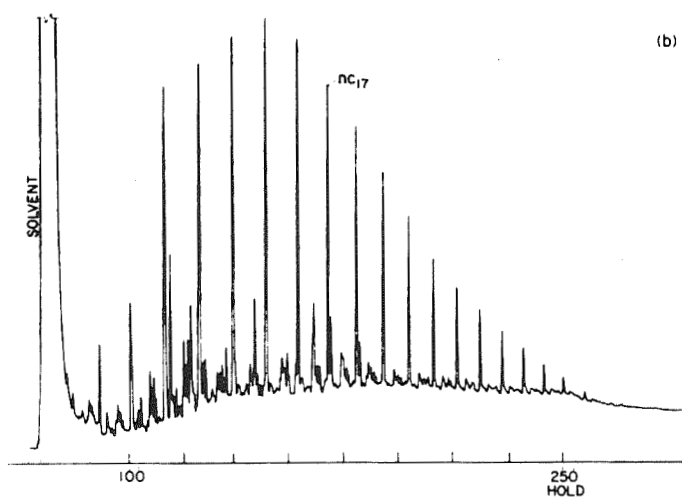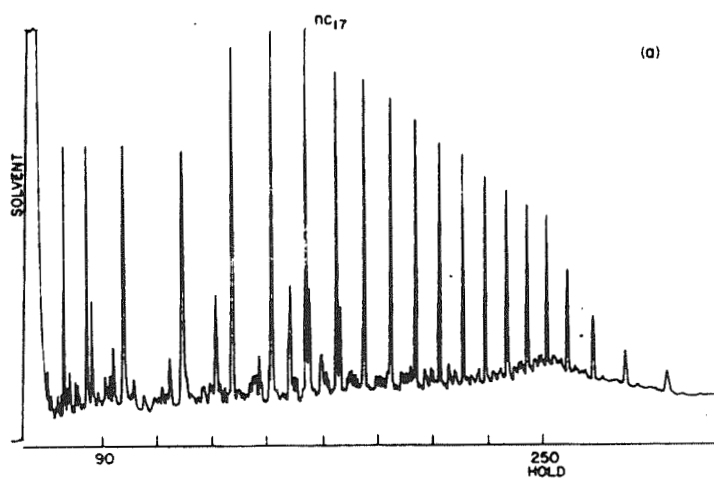
Fig. 27.–Aliphatic hydrocarbons extracted from the Raper Mine Edale Shale. Same conditions as Fig. 16.
   (a) Total aliphatic hydrocarbons
   (b) Branched-cyclic hydrocarbons from molecular seiving

(a)

(b)

nc_17

PRISTANE
RETENTION
TIME

TEMPERATURE, °C

SOLVENT

SOLVENT

90

100

200

90

100

200
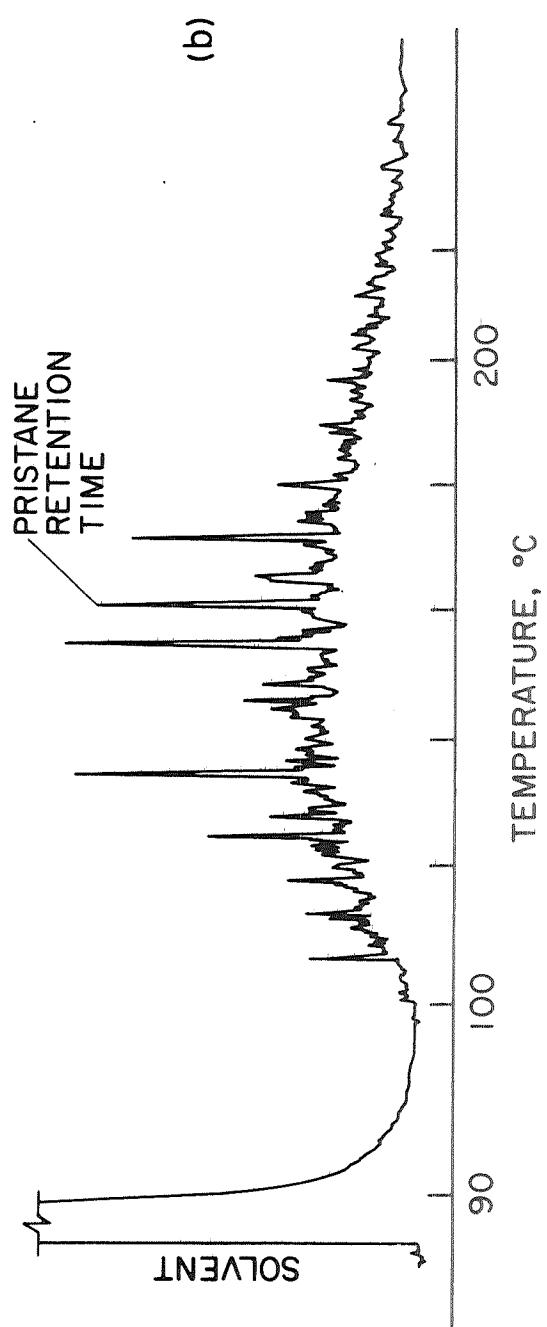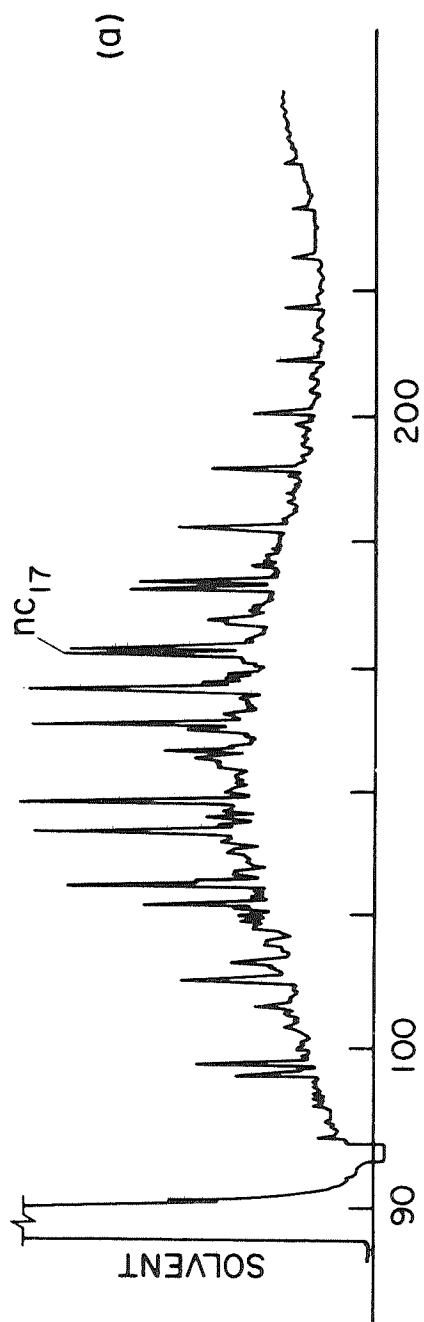
Fig. 28.–Infrared spectra of bitumens genetically related to the lower Carboniferous Limestone

WAVELENGTH, microns

1. BENZENE METHANOL SOLUBLE PART
   OF THE "ELATERITE" OIL

2. BENZENE METHANOL EXTRACT OF
   THE LOWER CARBONIFEROUS
   LIMESTONE

3 BENZENE METHANOL EXTRACT OF
   THE BLACK, SOLID BITUMEN

4. BLACK SOLID BITUMEN AS KBr PELLET

FREQUENCY, (cm⁻¹)
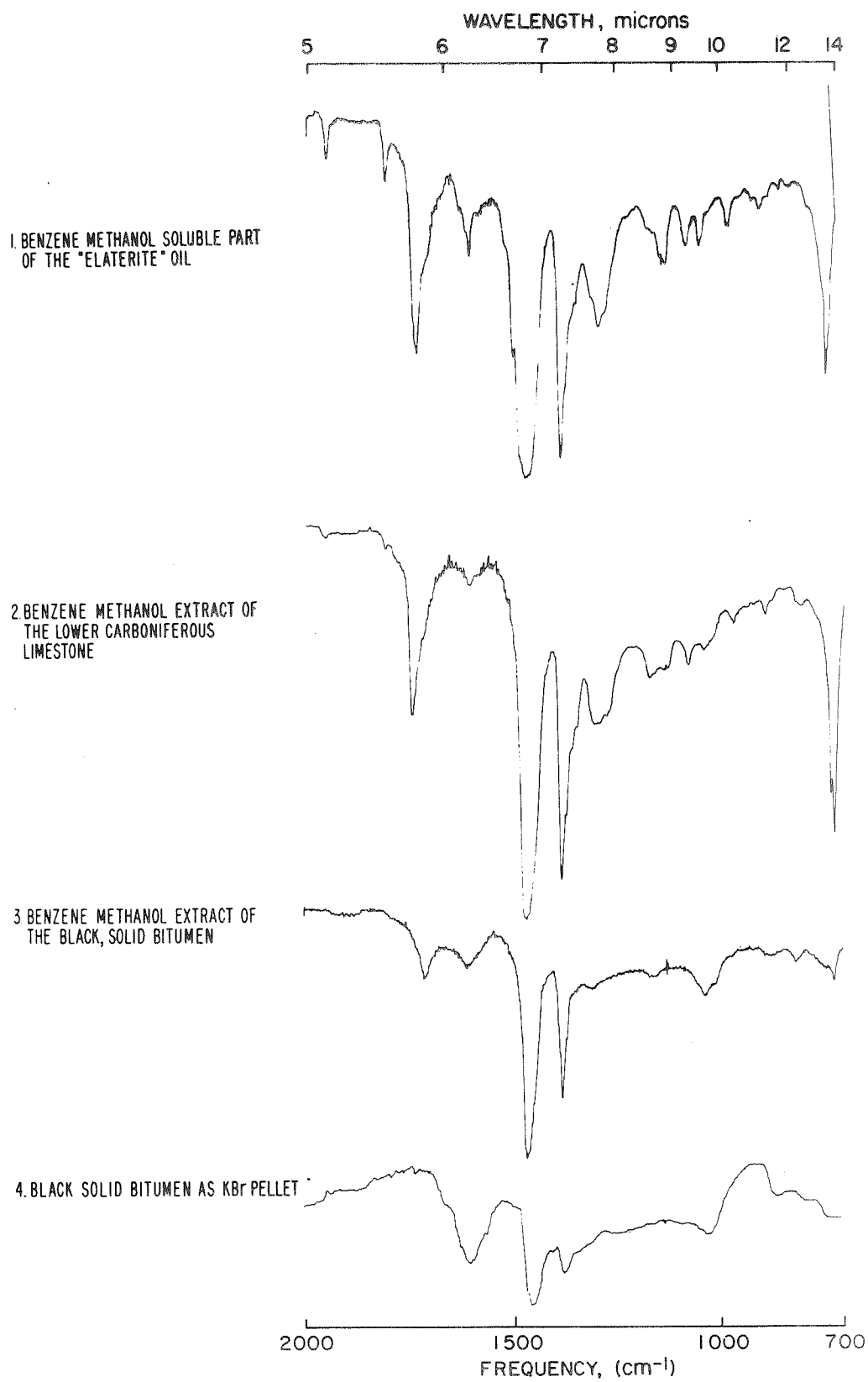
Fig. 29.–Aliphatic hydrocarbons extracted from the Lower Carboniferous Limestone. Same conditions as Fig. 26(b).
(a) Sample I-L: Boulder bed limestone, Treak Cliff
(b) Sample II-L: Massive limestone, Treak Cliff
(c) Sample III-L: Windy Knoll quarry

Figure showing three gas chromatograms (a), (b), and (c), each plotted as detector response versus TEMPERATURE, °C. Each trace is labeled SOLVENT at the left and nC₁₇ (nC_{17}) at a prominent peak, with the temperature axis marked at 100 and 250 HOLD.
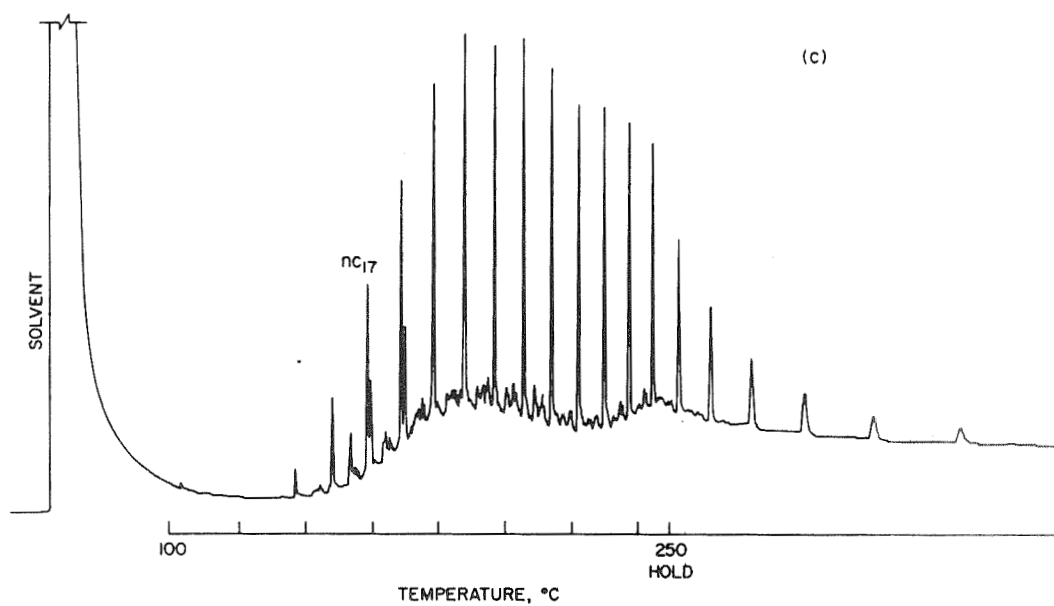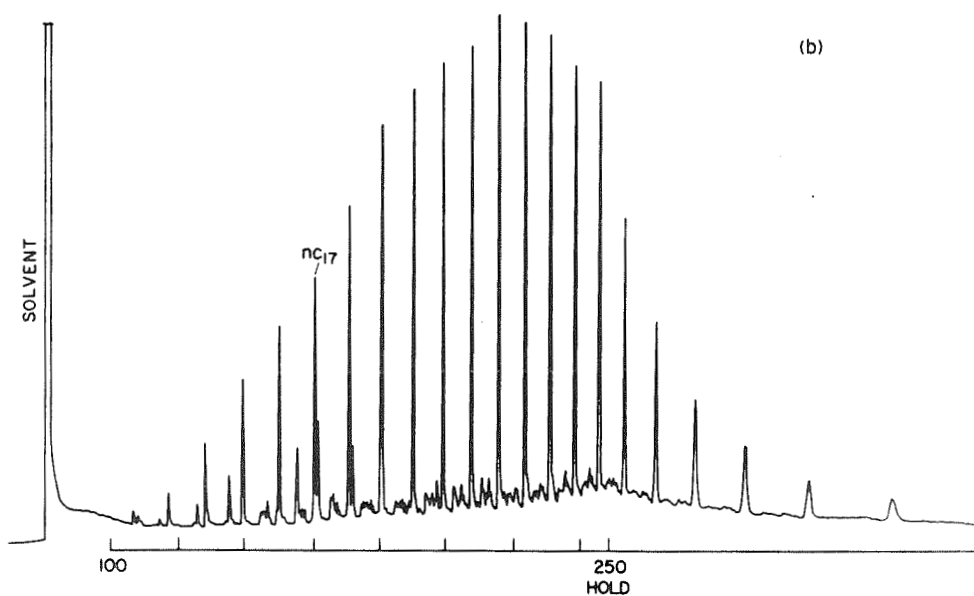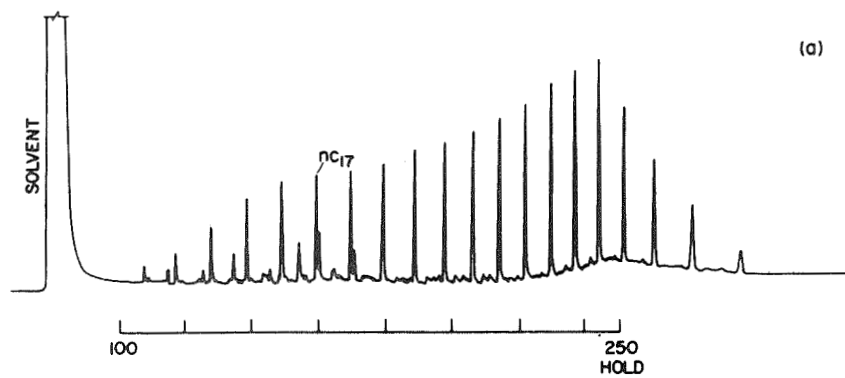
Fluorite

Extractable organic material in the purple fluorite yields an infrared spectrum suggesting a composition of low molecular weight carbonyl-containing compounds. The aliphatic hydrocarbons isolated from the first sample of purple fluorite exhibit a bimodal distribution pattern, with one maximum at nC_{17} and another at nC_{27} (Fig. 30). That of the aliphatics from the second sample is also bimodal, but the nC_{27} mode has a smaller intensity relative to the nC_{17} mode. Hydrocarbons exhibiting a distribution maximizing only at nC_{17} were isolated from the third sample. Insufficient material was extracted from the white fluorite for an infrared spectrum. The aliphatic hydrocarbons isolated from both samples have the same distribution pattern, which range from nC_{13} to nC_{32} and maximized at nC_{27} (Fig. 31).

Hardstoft, Eakring, and Plungar Crude Oils

The infrared spectra of the Hardstoft and Eakring crude oils are less complex than those of the extractable matter in either the limestones or the shales: they suggest that the oils are composed largely of aliphatic hydrocarbons, with minor amounts of oxygenated and aromatic material (Fig. 25 (5)). The aliphatic hydrocarbons in these two oils are almost identical: straight chain isomers dominate, ranging from C_{10} to C_{25} and maximizing at C_{13} (Fig. 32).

The Plungar crude oil yields an infrared spectrum indicating a much larger proportion of aromatic compounds than is present in the other two oils (Fig. 25 (6)). The aliphatic hydrocarbons from this oil are also different, containing a much larger proportion of branched-cyclic isomers which are the dominant compounds below nC_{17} (Fig. 32 (c)).

Brown Bitumen

About 3.4% of the brown bitumen is soluble in organic solvents. The infrared spectrum of this material indicates that long-chain aliphatic hydrocarbons are prominent constituents,

Fig. 30.–Aliphatic hydrocarbons extracted from the purple Treak Cliff Cavern fluorite. Same conditions as Fig. 26 (a, b)
    (a) Sample I-F sonicated once with benzene-methanol
    (b) Sample II-F sonicated twice with benzene-methanol
    (c) Sample III-F sonicated three times with benzene-methanol

(a)

(b)

(c)

nC_{17}

nC_{27}

SOLVENT

90   100   200

TEMPERATURE, °C
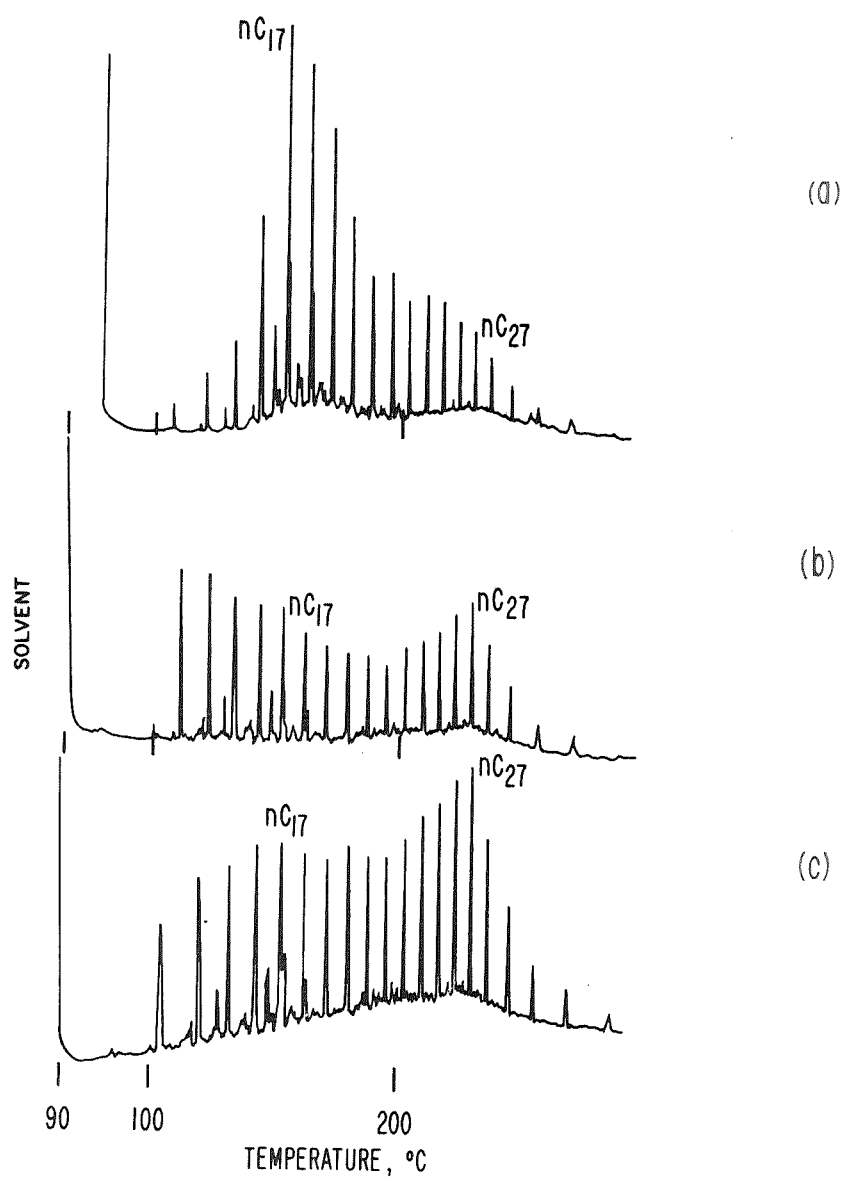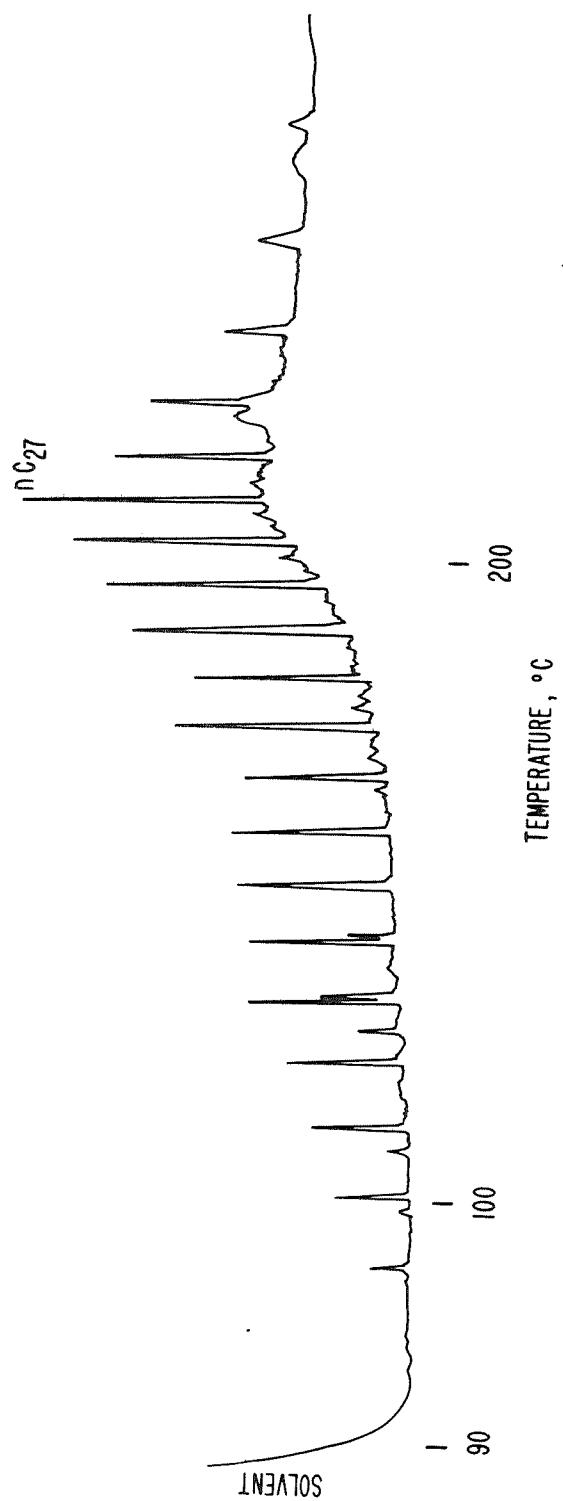
Fig. 31.–Aliphatic hydrocarbons extracted from the white, Treak Cliff Cavern fluorite. Same conditions as Fig. 26 (b)

Fig. 32.–Aliphatic hydrocarbons isolated from the Millstone Grit crude oils. Same conditions as Fig. 26 (c)

(a) Hardstoft Oil
(b) Eakring Oil
(c) Plungar Oil

TEMPERATURE, °C
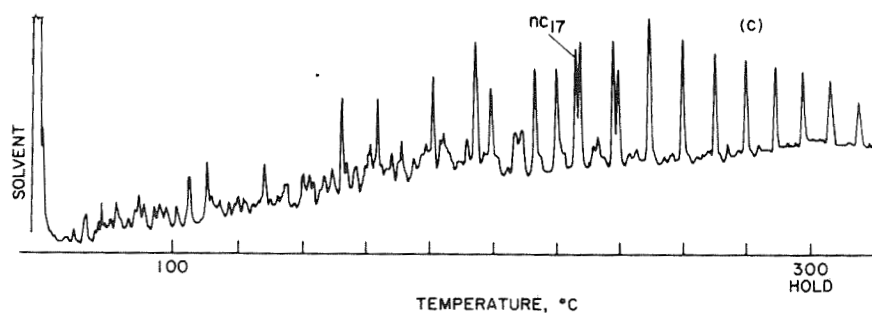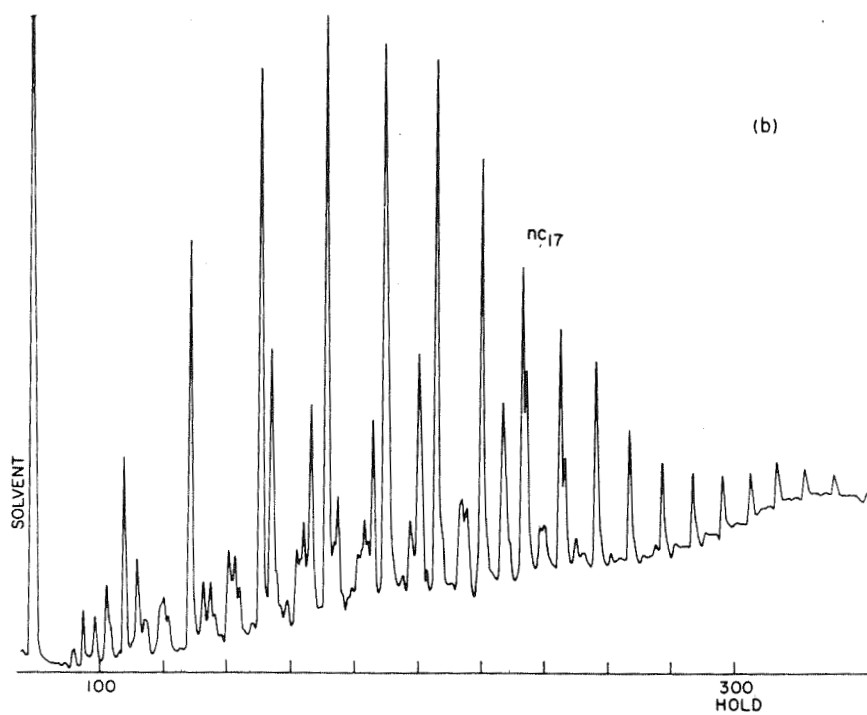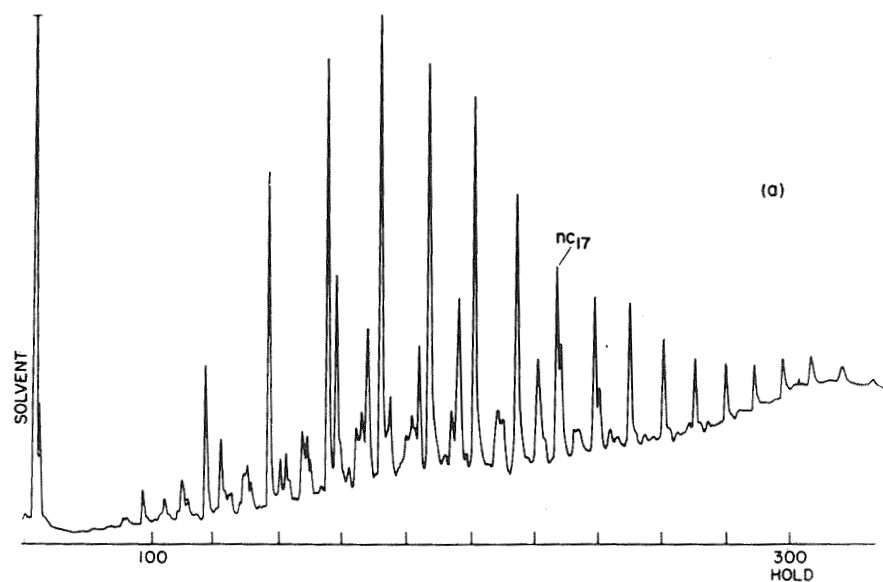
as well as some carbonyl-containing compounds (Fig. 25 (4)). The aliphatic hydrocarbon

fraction isolated from the extractable organic matter contains isomers ranging from C_{11} to

C_{22}, and maximizing around nC_{15} (Fig. 33). Confirmatory mass spectrometry shows that

the C_{16}, C_{18}, and C_{19} isoprenoid isomers are present (Pering and Ponnamperuma, 1968),

but phytane could not be detected.

The infrared spectrum of the brown bitumen indicates that it is composed largely of

aromatic and some oxygenated compounds (Fig. 25 (3)). However, its elemental compo-

sition indicates that it is intermediate between aromatic and aliphatic in composition and

contains moderate amounts of sulfur (Table 2). Low temperature pyrolysis of the insol-

uble part of the brown bitumen yields a set of products whose combined infrared spectrum

indicates the presence of a complex series of oxygenated and sulfonated aromatic com-

pounds (Fig. 25 (2)). Heating the bitumen to $160°$ C released hydrocarbons similar to

those extracted from the unheated sample (Fig. 34 (a)). Further heating to $260°$ C released

a more complex, high-boiling mixture of hydrocarbons (Fig. 34 (b)), while heating to $310°$ C

caused marked appearance of a new homologous series of hydrocarbons, which are probably

cracking products (Fig. 34 (c)). Acrid, sulfurous smelling material began forming at about

$180°$ C and thus was concentrated in the $270°$ C fraction. This material eluted from an

alumina column only with methanol, suggesting that the sulfur-containing compounds are

very polar.

Elaterite Oil

Moderately strong absorption in the carbonyl and long-chain methyl regions of the

infra-red spectrum of the Elaterite oil suggests that it is composed primarily of aliphatic

hydrocarbons and carbonyl compounds (Fig. 28 (1)). This composition is supported by

elemental analysis of the oil, which shows the highest percentage of hydrogen of the three

bitumens (Table 3). About 1% of the aliphatic hydrocarbons are unsaturated and yield
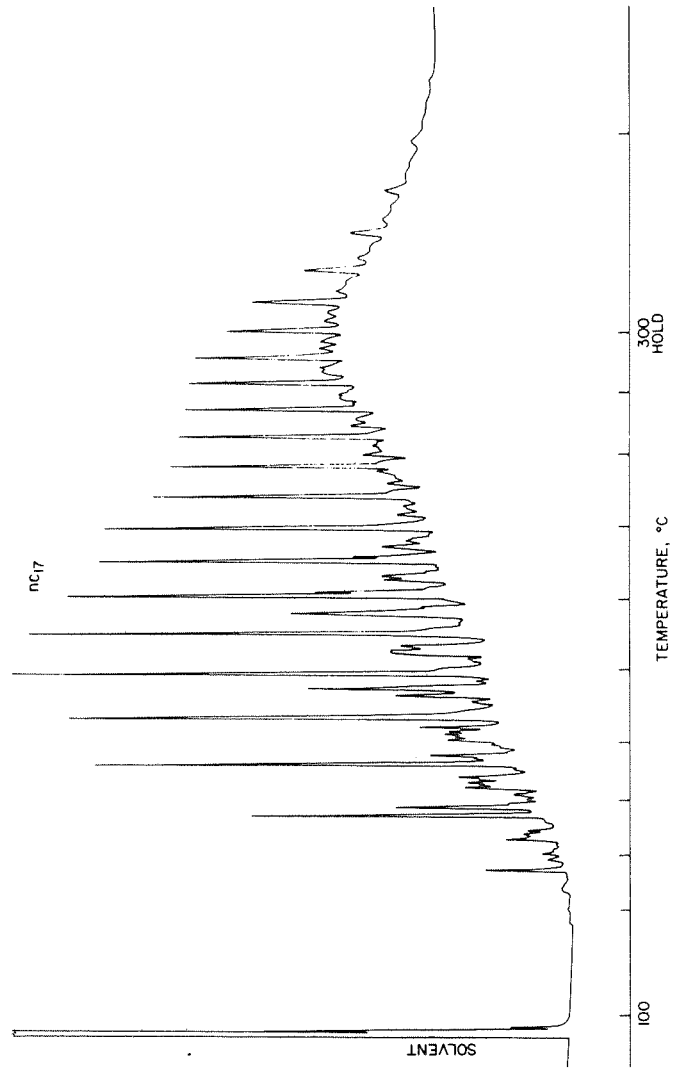
Fig. 33.—Aliphatic hydrocarbons extracted from the brown bitumen. Same conditions as Fig. 26 (b)

TABLE 2

ELEMENTAL COMPOSITION OF THE THREE BITUMENS IN THE WINDY KNOLL DEPOSIT

	Brown Bitumen	Black Bitumen	Elaterite Oil
C	87.91	86.16	84.30
H	9.88	7.43	12.71
N	0.07	0.53	0.86
S	1.64	1.01	0.47

Fig. 34.--Aliphatic hydrocarbons extracted from the brown bitumens after pyrolysis. Same conditions as Fig. 26 (c)
  (a) After heating to 165° C
  (b) After heating to 260° C
  (c) After heating to 310° C

(a)

(b)

(c)

TEMPERATURE, °C
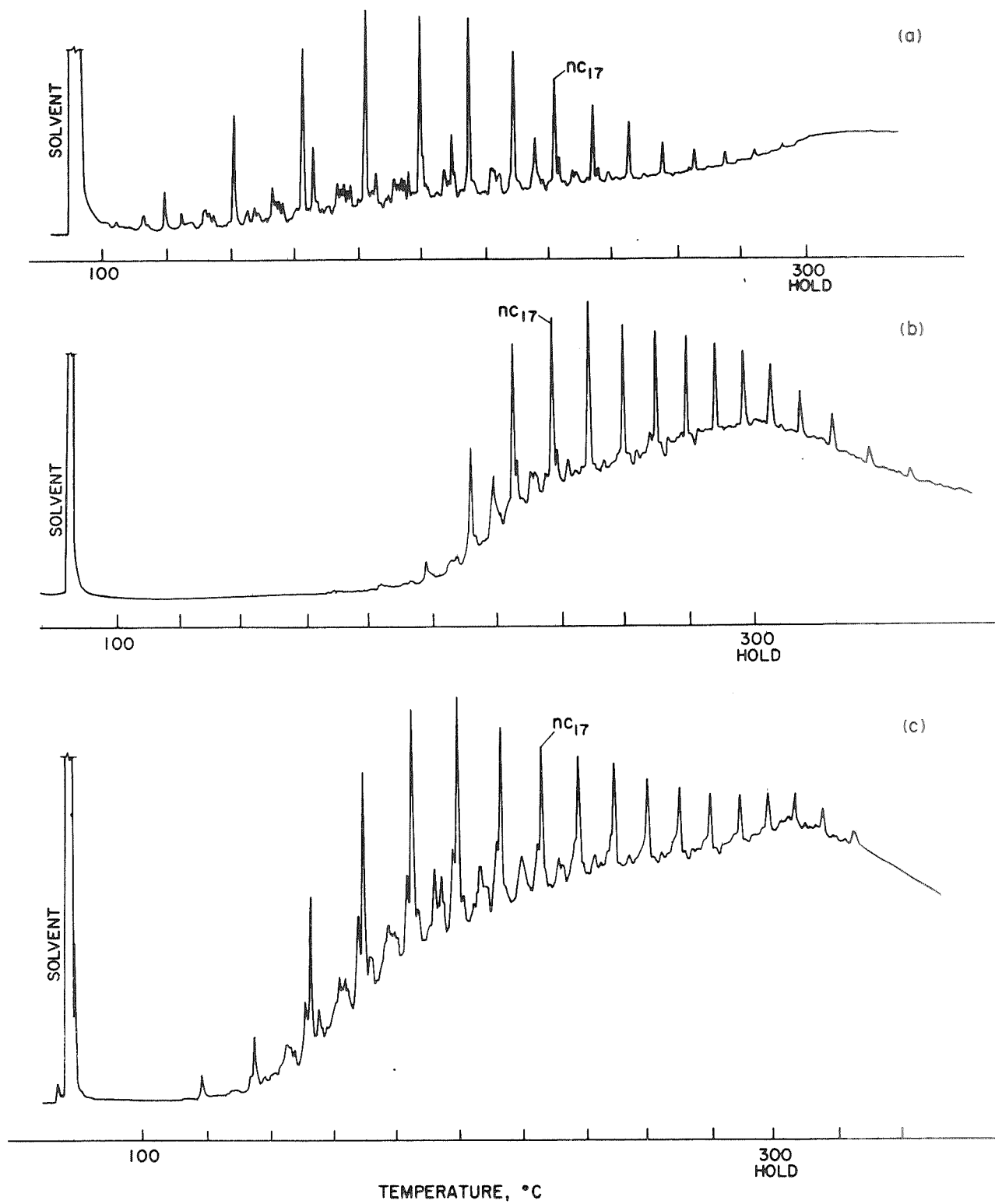
an infrared spectrum absorbing at 965 cm^{-1}, which is indicative of trans-substituted double bonds. The saturated hydrocarbons are a complex mixture of predominantly high molecular weight isomers which are very similar to those isolated from the black bitumen (Pering and Ponnamperuma, 1968).

Black Bitumen

The infrared spectrum of the extractable material in the black bitumen characterizes it as a mixture of aromatic, aliphatic and oxygenated compounds (Fig. 28 (3)), while the insoluble fraction is predominantly aromatic (Fig. 28 (4)). The high degree of aromaticity of this bitumen is also indicated by its elemental composition, which shows the lowest percentage of hydrogen of the three bitumen samples (Table 2). The aliphatic hydrocarbons isolated from the bitumen are a complex mixture of high molecular weight isomers which cannot be resolved on existing gas chromatographic columns (Fig. 35). The most striking characteristic of this mixture is its lack of a definitive homologous series of straight-chain isomers.

Discussion

Field geologic relationships, as well as petroleum migration and accumulation patterns in this area suggest possible sources for the bitumes at Windy Knoll. The black bitumen, which is consistently associated with calcite in the main deposit, resembles the black-colored organic matter which is distributed throughout the limestone as tiny particles and which concentrates in masses as the carbonate matrix dissolves or recrystallizes. Black bitumen of this type has been observed in limestone hosting the Mississippi Valley ore deposits (Brecke, 1962) where it is concentrated in a dark zone along the lower contact of fluorite ore with the host limestone, and as halos where the bitumen was displaced into pores and voids in the banded ore.

Fig. 35.–Aliphatic hydrocarbons extracted from the black bitumen
(a) same conditions as Fig. 26 (b)
(b) same conditions as Fig. 26 (c)
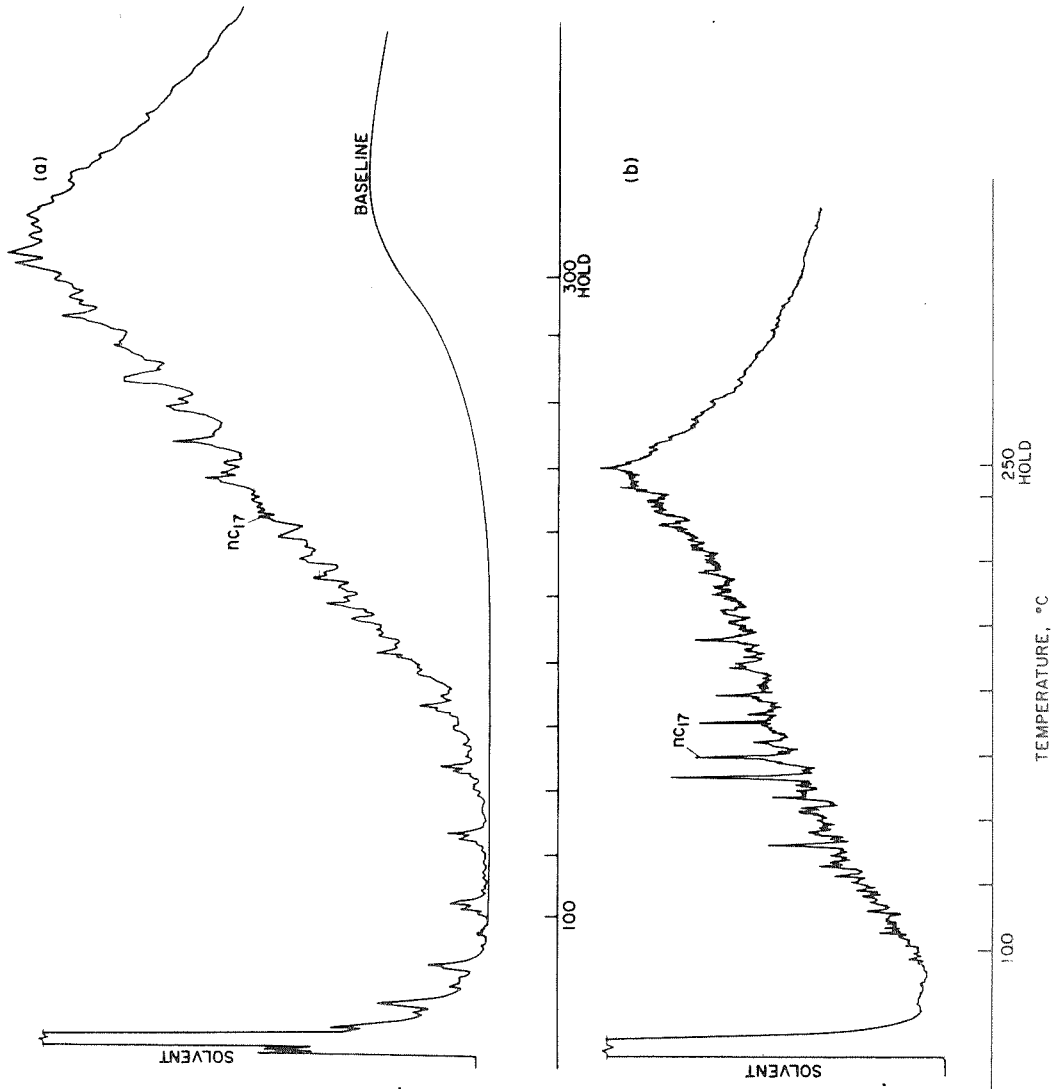
The liquid bitumen, or Elaterite, may well be an analogous, but highly mobile fraction which concentrates in structures channeling migrating fluids through the limestone. Vacuoles of a similar, but solid, green bitumen in the limestone fragments suggest that the limestone hosting this deposit may have been very bituminous, and that part of the oil may have a very local origin.

The brown bitumen, which was apparently extruded into pre-existing limestone cavities, could have migrated from the overlying Edale Shale as did oil elsewhere in the Millstone Grit rocks. Preserved flow structures in this bitumen indicate that it was a viscous fluid at the time of deposition: the striking shape of the rods brings to mind the behavior of oil entering a water saturated porous rock. In this interface phenomenon known as "fingering," fluid migrating in the porous medium has a front of protruding streamers of fluid trending perpendicular to it (Collins, 1961). A somewhat similar movement involving the brown bitumen might have resulted in "fingers" which solidified to rock. The orientation of the pockets of rods to each other might be divergent because large fragments in addition to fine grained material were involved.

The organic compounds in the mineral fluorite might be considered a key to the effect of the hydrothermal fluids on the organic matter, as these represent the compounds in solution with which the fluorite was in contact at the time of crystallization. The distribution of hydrocarbons in this mineral is remarkably similar to that of the hydrocarbons in the Castleton Edale Shale (purple fluorite) and to that of the limestone (white fluorite). The bimodal distribution pattern observed in the purple fluorite subjected to minimal crushing suggests that sequential mixing of the hydrocarbons from both sediments has occurred, but there is no evidence that the hydrocarbons have been otherwise altered. The apparent highly polar nature of the total extractable organic matter in the fluorite might be due to a chemical alteration process, such as oxidation or hydrolysis; but just as likely, it may be due to selective adsorption of oxygen-containing compounds onto the fluorite crystal surfaces.

The changes in organic matter caused by simple migration from a source rock to a secondary deposit are still controversial (Welte, 1965; Baker, 1960), but some changes that may have occurred in the Castleton area can be indirectly defined by comparing the Millstone Grit crude oils with the Edale Shale organic matter. Differences between the composition of the Hardstoft and Eakring oils and the Castleton shale suggests that the main transformation would be a selective loss of oxygen-containing and aromatic compounds to yield a paraffin-rich mixture. Small losses of higher molecular weight hydrocarbons, or their breakdown to smaller molecules in the reservoir, are possible explanations for the slightly higher content of volatile hydrocarbons in these oils relative to the shale. The seemingly anomalously high branched-cyclic isomer content of the Plungar crude oil may signify that additional alteration processes can occur, but this composition change could also be due to lateral facies changes in the source rock. For instance, the hydrocarbons from the Raper Mine shale also exhibit an increase in branched-cyclic relative to straight-chain isomers.

The chemical characteristics of the brown bitumen agree well with the geologic and chemical evidence for its origin. The distribution pattern of the bitumen aliphatic hydrocarbons closely resembles that of its postulated source rock, the Edale Shale, as well as those of the Millstone Grit oils. The originally high viscosity of the bitumen suggests that it did not migrate far enough to lose the more asphaltic components. Hydrothermal fluids apparently interacted with this bitumen simultaneously with or just after it had solidified, but before the bitumen became coated with oil that would have inhibited adhesive crystal growth on its solid surface. As with the fluorite, this interaction had no effect on the aliphatic hydrocarbon distribution patterns. However, these fluids could have caused an increase in the rate of auto-polymerization of the then viscous vitumen to such a point that concurrently forming flow structures were preserved in the hardening material. Since this bitumen is still reactive to acidic solutions, an acid-catalyzed polymerization could be postulated.

If the brown bitumen is classified according to its physical properties, it is a "pyrobitumen" (Table 3). A property often used in characterizing bitumens according to this classification is their H/C ratio (Table 4). On this basis, the brown bitumen resembles Albertite, another bitumen which occurs in shale (King, 1963). The main difference between these bitumens is that the Albertite is black: perhaps it represents a more advanced polymerization product than the brown bitumen.

The general chemical characteristics of the black bitumen and the Elaterite are those which would be predicted on the basis of geologic evidence that they are derived from the Lower Carboniferous Limestone. According to their physical properties (Table 3), the Elaterite resembles a "petroleum" or "mineral wax," and the black bitumen a "non-asphaltic pyrobitumen"; and on the basis of their H/C ratios, they are similar to ozocerite and a coal-type substance, respectively. These two classifications conform well with the concept that these bitumens represent liquid and solid fractions of the limestone organic matter.

The distribution patterns of the aliphatic hydrocarbons isolated from the black bitumen and the Elaterite are essentially the same, and are strikingly different from those extractable from the limestone around Castleton. This implies that the hydrocarbons, which presumably are derived from the limestone, have been altered. Since it has already been shown that hydrothermal fluids did not alter aliphatic hydrocarbons elsewhere in this area, it seems reasonable to exclude hydrothermal alteration from consideration here.

A possible explanation is that the alkanes have been degraded by bacteria. Soil bacteria are known to alter crude oils by decreasing the n-paraffin content (Davis, 1967) and specific evidence for alteration of petroleum in the reservoir has recently been reported (Winters and Williams, 1969). Gas chromatograms of the aliphatic hydrocarbons from unaltered and altered parts of the oil fields studied by Winters and Williams show that complex distribution patterns similar to those in the black bitumen and Elaterite

SOLUBILITY OF BITUMENS IN CARBON DISULPHIDE

SOLUBLE BITUMENS

INSOLUBLE BITUMENS

LIQUID

SOLID

FUSIBLE

INFUSIBLE

PETROLEUM

1. ALL CRUDES
2. OIL SEEPS

DIFFICULTLY FUSIBLE

FUSIBLE

PYROBITUMENS

MINERAL WAX

ASPHALT

ASPHALTITES

OXYGEN FREE

OXYGEN CONTAINING

3. OZOCERITE
4. MONTAN WAX
5. HATCHETTITE
6. SCHEERERITE

7. BERMUDEZ PITCH
8. TABBYITE
9. LIQUID GILSONITE
10. ARGULITE

11. GILSONITE
12. GRAHAMITE
13. GLANCE PITCH

ASPHALTIC PYROBITUMENS

NON-ASPHALTIC PYROBITUMENS

14. WURTZILITE
15. ELATERITE
16. ALBERTITE
17. IMPSONITE
18. INGRAMITE

19. PEAT
20. LIGNITE
21. COAL

TABLE 3
CLASSIFICATION OF BITUMEN TYPES

TABLE 4

THE H/C ATOMIC RATIO OF THE BITUMENS AT WINDY KNOLL
AS COMPARED WITH SOME OTHER NATURAL BITUMENS

Hydrocarbon	H/C Atomic Ratio
1. Ozocerite	1.89 - 1.96
2. Elaterite Oil	1.81
3. Ingramite	1.62
4. Wurtzilite	1.59 - 1.60
5. Gilsonite	1.42 - 1.47
6. Brown Bitumen	1.35
7. Albertite	1.24 - 1.32
8. Black Bitumen	1.04
9. Coal	0.99
10. Bituminous Coal	0.80
11. Anthracite	0.56

Source: Adapted from Hunt, Stewart, and Dickey, 1954

are generated. Another aspect of these altered oils is that they contain up to four or five

times as much nitrogen as the unaltered oils. Winters and Williams suggest that such high

nitrogen content is due partly to amino acids derived from proteinaceous material normally

produced by paraffin-oxidizing micro-organisms. Nitrogen compounds in petroleum are

usually associated with aromatic molecules such as porphyrins or high molecular weight

asphaltenes, yet the highest concentration of nitrogen in the Windy Knoll deposit occurs

in the most paraffinic bitumen, the Elaterite oil, which contains more than eight times

as much nitrogen as its paraffinic analogue, ozocerite (Table 5).

Another indication of bacterial activity is the presence of unsaturated hydrocarbons

in the Elaterite. Unsaturated hydrocarbons are produced during microbial metabolism

and have been associated with the presence of microbes in other naturally occurring

organic matter (Douglas, Eglinton and Maxwell, 1969). Polymerization of unsaturated

hydrocarbons could explain the high molecular weight distribution pattern which is so

characteristic of the saturated hydrocarbons in these two bitumens. Furthermore, the

elasticity for which the Elaterite is so well known could be the result of cross-linking of

the unsaturated material as it polymerizes, or it may be the property of a residual biologic

TABLE 5

THE NITROGEN CONTENT OF THE WINDY KNOLL BITUMENS
COMPARED WITH THAT OF SOME NATURAL BITUMENS

Bitumen	Nitrogen Content
Elaterite	0.86
Black bitumen	0.53
Brown bitumen	0.07
Ozocerite[1]	0.10
Bell Creek Crude[2]	
Oil Unaltered	0.04
Altered	0.14

[1]Hunt, Stewart, and Dickey (1954)
[2]Williams and Winters (1969)

elastic gel produced by the bacteria. The brown bitumen would not be affected by this

type of alteration because it is impervious to fluids, while the black bitumen, which is

a composite of fine particles, is quite permeable and would be affected. Although it is con-

ceivable that alteration of the hydrocarbons took place during suberial erosion of the lime-

stone in late Carboniferous or Permian times, it seems doubtful that the geologically

fragile, unsaturated hydrocarbons would survive. These considerations, coupled with the

fact that conditions in the deposit are now conducive to microbial growth, suggest that

alteration of the bitumens is a very recent phenomenon, and may still be taking place.

Conclusions

A postulated geologic and geochemical history for the bitumen deposit at Windy

Knoll which is compatible with the findings of this study is summarized below.

A. Fluids began migrating along the boulder bed unconformity possibly because a

fluid pressure gradient developed at Odin Rake (Fig. 36 (a)).

B. These fluids partially dissolved the limestone along the unconformity, releasing

organic matter from the carbonate matrix. As the fluids passed through the topographic

high at Windy Knoll, the oil fraction was trapped along the top and the black bitumen,
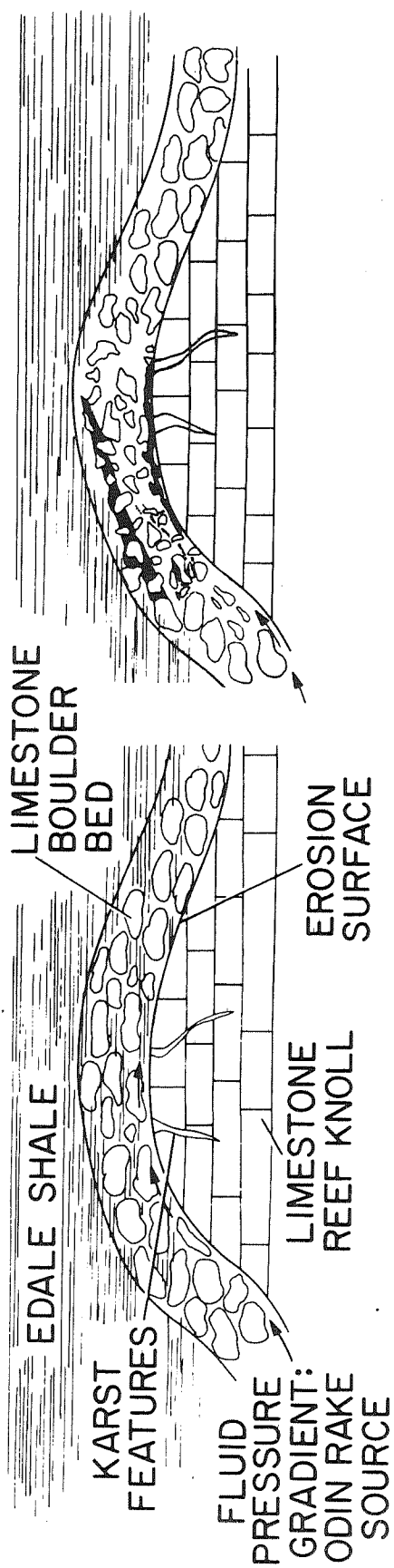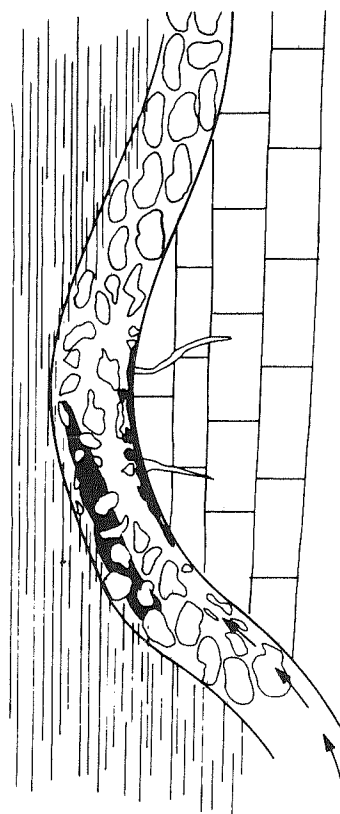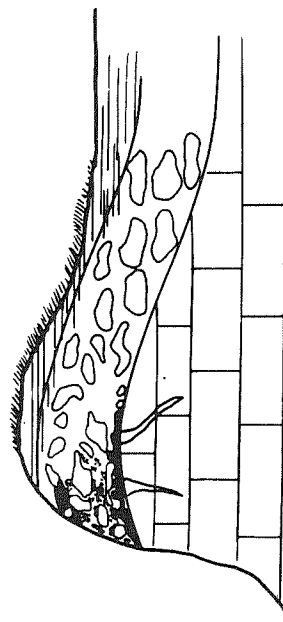
Fig. 36.–Schematic summary of the sequence of events hypothesized to have led to the formation of the deposit at Windy Knoll

being heavier than water, concentrated along the bottom (Fig. 36 (b)).

C. Asphaltic bitumen released as the Edale Shale compacted began flowing into the same trap around fragments of undissolved limestone and concentrated between the other two bitumens in the aqueous layer. Warm hydrothermal fluids, coupled perhaps with high hydrogen sulfide concentrations in the shale connate water, catalyzed auto-polymerization of this bitumen and then began to precipitate marcasite, fluorite, etc., around the solidified forms (Fig. 36 (c)).

D. Erosion of the Edale Shale and recent quarrying of the limestone exposed the Windy Knoll deposit. Exposure to the atmosphere, and flow of ground water through the bitumen created favorable conditions for bacterial growth in the more permeable forms (Fig. 36 (d)).

This geologic history is quite different from that previously postulated by Mueller. The history presented here is based in part on the fact that little chemical or geologic evidence for thermal alteration processes could be found, and in part on indirect evidence that viable organisms are an active part of the present geologic environment of Windy Knoll. It is difficult to say at this time to what extent these results can be applied to other bitumens such as those outlined in Chapter II. However, they do suggest that microbial alteration processes in hydrothermal environments deserve much more attention than they have attracted in the past, and that perhaps too much emphasis has been placed on purely thermal reactions.

CHAPTER V

SYNOPSIS

Several hydrocarbon characteristics which might serve as criteria for the abiogenic origin of naturally occurring organic matter have been presented in this study. These were defined by reviewing the types of hydrocarbons reported in the literature to be synthesized from simple, carbon containing gases and selecting the characteristics of these types which differ from those commonly observed in geologically occurring hydrocarbons of biological origin. To summarize, these characteristics are:

1. A complex mixture of aliphatic hydrocarbons predominantly composed of cyclic, highly branched isomers and exhibiting a symmetrical, hump-like gas chromatographic distribution pattern.

2. A simple mixture of aliphatic hydrocarbons which yields a gas chromatographic distribution pattern marked by a repetitive sequence of monomethyl branched paraffin and olefin isomers between intense n-alkane peaks, the intensity of all the peaks decreasing with molecular weight.

3. A mixture of aromatic hydrocarbons consisting predominantly of two and three ring arenes containing an even number of carbon atoms.

4. A positive correlation of the C/H ratio of the hydrocarbons (all types) with synthesis temperature.

If the abiogenicity of a particular organic mixture can be established, the above listed hydrocarbon characteristics appear also to be capable of providing information about the conditions under which the mixture was synthesized. It appears, for instance, that the very complex mixtures of isomers (characteristic 1) are consistently the product of syntheses

involving methane as the main carbon containing reactant. On the other hand, simpler mixtures in which n-alkanes predominate (characteristic 2) are associated with syntheses based on the reactant, carbon monoxide. The presence of aromatic hydrocarbons composed predominantly of even numbers of carbon atoms may likewise suggest that methane was the original reactant, but more needs to be known about the types of aromatics produced from carbon monoxide before this conclusion can be considered too seriously. Additional information concerning the temperatures involved in a particular synthesis appear to be furnished by the relative distributions of the various hydrocarbon types. For instance, the curve in Fig. 1 suggests that if the hydrocarbons in an organic mixture are only aromatic, the mixture was probably synthesized at temperatures higher than 500° C; however, if it contained exclusively aliphatic isomers, it could be concluded that temperatures never or rarely exceeded 400° C.

The latter half of this thesis study has been concerned with assessing the usefulness of the aliphatic hydrocarbon characteristics in determining the origin of bitumens in unusual geologic environments. At first, the results of the brief survey of unusual bitumens seems to suggest that the characteristic based on a complex mixture of cyclic aliphatic hydrocarbon isomers is far too common to apparently biologically derived bitumens to be a useful criterion for abiogenicity. However, the detailed study of the Windy Knoll bitumen deposit shows that the resemblance between these apparently altered biological hydrocarbons and the synthetic mixtures can be superficial; although both the Windy Knoll and the synthetic hydrocarbons are very complex mixtures of predominantly cyclic isomers, those at Windy Knoll consist of much longer chained, less branched molecules; contain unsaturated bonds; and yield a very assymetric, hump-like distribution pattern that maximizes at much higher molecular weight ranges than does the synthetic material. Other evidence is presented that indicates that the complex hydrocarbon isomer mixtures at Windy Knoll are the result of microbial oxidation of these bitumens, rather than of

alterations associated with the moderately warm temperature geologic ore forming processes known to have been active in the area.

Thus, on the basis of the Windy Knoll study alone, it appears that the characteristics of synthetic aliphatic hydrocarbons still can be considered useful in indicating abiogenicity providing that close attention is paid to the subtle differences which can exist between them and altered hydrocarbons of biological origin. And, close attention is paid to the possibility of microbial growth in the organic matter in question. But, similar or even more detailed studies of the other bitumens containing complex mixtures of aliphatic hydro-carbons are necessary to show whether or not the findings at Windy Knoll can be generalized to explain and describe all such occurrences.

A useful example of the way information provided by hydrocarbons can be interpreted is available in the recent findings concerning the Murchison carbonaceous chondrite (Kven-volden, et al., 1970).

The abiogenic origin of this organic matter can be fairly well established on the basis of carbon isotope ratios, the presence of racemic, as well as non-protein amino acids, and the following hydrocarbon characteristics.

1. The alkanes are predominantly mono and bicyclic isomers with short chain branches which upon gas chromatography, yield a distribution pattern resembling a Gaussian curve.

2. The aromatic hydrocarbons are predominantly two and three ring arenes composed of even numbers of carbon atoms (Pering and Ponnamperuma, 1971).

3. The approximate ratio of the types of hydrocarbons (aliphatic, aromatic and un-saturated) is 10:9:1.

The evidence presented in this thesis suggests that these findings can be interpreted to indicate that methane was probably the most predominant carbon containing reactant from which organic matter in the meteorite was formed. This seemingly simple piece of information is important because evidence from previous meteorite studies (largely involving contaminated

samples) suggested that a Fischer-Tropsch reaction involving carbon monoxide was the principal source of the organic matter. The third observation listed above suggests that the temperature history of this methane rich reaction mixture involved brief exposures to temperatures perhaps as high as 900° C, but also involved considerable residence time at lower temperatures since over half the hydrocarbons are aliphatic. (A plausible lower limit for the temperature might be set at 300° C since only the Fischer-Tropsch type reactions and irradiation syntheses yield hydrocarbons at lower temperatures.) This information provides a new starting point for designing model synthesis experiments to replicate the extraterrestrial processes which formed these compounds. And these experiments in turn will surely add to our capability to recognize the chemical characteristics of abiogenic organic material.

APPENDIX

The amount of water which could be retained in the outer portions of the earth, while other gases accumulated in the atmosphere, can roughly be estimated if it is assumed that the surface of the earth was as cool, or cooler than it is today (Meadows, 1970). A reasonable form for any retained water would be either as a serpentine-like mineral such as chlorite or as amphiboles, such as hornblende (or biotite) [$(Mg_6Si_4O_{14})(H_2O)_4$: 552g/mole; and $NaCa_2(Mg,Fe,Al)_5(Si,Al)_8O_{23}(H_2O)$: 800 g/mole, respectively].

The amount of water which would have to be retained as hydrated silicates would be similar to that estimated by Rubey for the total amount of water released on the surface of the earth: 1.5×10^{24} g (Rubey, 1951). If serpentine were the predominant mineral, the amount of rock necessary to retain this amount of water would be:

$$\frac{1.5 \times 10^{24} \text{ g } H_2O}{72 \text{ g } H_2O \text{ / mole rock}} \quad (552 \text{ g/mole}) = 11.4 \times 10^{24} \text{ g rock}$$

Or, if hornblende were the predominant mineral, the analogous computation would yield 6.2×10^{25} g rock.

If it is assumed, for the purpose of calculation, that this rock is distributed as a shell around the earth, the thickness of the equivalent slab will provide an estimate of the depth of rock necessary to retain this amount of water, as: (area)(height)(density) = mass of rock area $\cong$ surface of the earth. For serpentine:

$$(5 \times 10^{18} \text{ cm}^2)(h \text{ cm})(3 \text{ g/cc}) \cong 11.4 \times 10^{24} \text{ g}$$

and the thickness of the shell $\cong$ 7.6 Km. For hornblende:

$$(5 \times 10^{18} \text{ cm}^2)(h \text{ cm})(3.2 \text{ g/cc}) \cong 6.7 \times 10^{25} \text{ g}$$

and the thickness of the shell $\cong$ 42.4 Km. Whether or not such depths are reasonable depends, of course, on the thermal gradient in the earth at this time. These calculations simply show

that it is possible that all water was initially retained as a hydrated layer perhaps 25 Km thick and composed of about 50% serpentine and 50% hornblende.

REFERENCES

Abraham, H. (1945) *Asphalts and Allied Substances.* New York: D. Van Nostrand Co.

Allen, W. V., and Ponnamperuma C. (1967) A possible prebiotic synthesis of monocarboxylic acids. *Currents in Modern Biology 1,* 24-28.

Asinger, F. (1968) *Paraffins, Chemistry and Technology.* London: Pergamon Press, Ltd., 89-181.

Bailey, E. H. (1959) Froth veins formed by immiscible hydrothermal fluids in mercury deposits, Calif., *Bull. of the Geol. Soc. Am. 70,* 661-664.

Ball, J. S., Whisman, M. L., and Wenger, W. J. (1951) Nitrogen content of crude petroleums, *Industr. Eng. Chem. 43,* 2577-2581.

Baker, E. G. (1960) A hypothesis concerning the accumulation of sediment hydrocarbons to form crude oil, *Geochim. et Cosmochim. Acta. 19,* 309-317.

Barghoorn, E. S., Meinschein, W. G., and Schopf, J. W. (1965) Paleobiology of a Precambrian shale, *Science 148,* 461-472.

Barnes, H. L., ed. (1967) *Geochemistry of Hydrothermal Ore Deposits.* New York: Holt, Rinehart and Winston, Inc., 587.

Barton, P. and Fenske, M. R. (1970) Hydrocarbon extraction of saline waters, *Ind. Eng. Chem. Process Des. Develop. 9,* 18-25.

Bateman, A. M. (1959) *Economic Mineral Deposits.* New York: John Wiley & Sons, Inc.

Belsky, T., Johns, R. B., McCarthy, E. D., Burlingame, A. L., Richter, W., and Calvin, M. (1969) Evidence of life processes in a sediment two and a half billion years old, *Nature 206,* 446-447.

Blumer, M. (1957) Removal of elemental sulfur from hydrocarbon fractions, *Anal. Chem. 29,* 1039-1041.

Brecke, E. A. (1962) Ore genesis of the Cave-in-Rock fluorspar district, Hardin County, Illinois, *Econ. Geology 57,* 499-535.

Breger, I. A., ed. (1963) *Organic Geochemistry.* New York: MacMillan Co.

Brooks, B. T. (1950) *The Chemistry of the Nonbenzenoid Hydrocarbons.* New York: Reinhold Pub. Corp.

Chang, S., Smith, J., Kaplan, I., Lawless, J., Kvenvolden, K., and Ponnamperuma, C. (1970) Carbon compounds in Lunar fines from Mare Tranquillitatis - IV. Evidence for oxides and carbides., *Geochim. Cosmochim. Acta, Proc. of the Apollo 11 Lunar Science Conf. 2,* 1857-1869.

Collins, R. E. (1961) *Flow of Fluids Through Porous Material.* New York: Reinhold Pub. Corp., 196-200.

Dauvillier, A. (1965) *Photochemical Origin of Life.* New York: Academic Press, 79.

Davis, D. R., and Libby, W. F. (1964) Positive-ion chemistry: high yields of heavy hydrocarbons from solid methane by ionizing radiation, *Science 144,* 991-992.

Davidson, C. F., and Bowie, S. H. W. (1951) I. On thucholite and related hydrocarbon-uraninite complexes, *Bull. Geol. Survey, Great Britain 3* No. 1.

Davis, J. B. (1967) *Petroleum Microbiology.* Amsterdam: Elsevier Pub. Co., 110.

Dayhoff, M. O., Lippincott, E. R., and Eck, R. V. (1964) Thermodynamic equilibria in pre-biological atmospheres, *Science 146,* 1461-1464.

Dons, J. A. (1956) Coal blend and uraniferous hydrocarbons in Norway, *Norsk Geologisk Tidsskrift 36,* 248-266.

Douglas, A. G., Eglinton, G., and Maxwell, J. R. (1969) The hydrocarbons of Coorongite, *Geochim. Cosmochim. Acta 33,* 569-577.

Dunham, K. C. (1967) Veins, flats and pipes in the Carboniferous of the English Pennines, in *Genesis of Stratiform Lead-Zinc-Barite-Fluorite Deposits; Econ. Geology* Mono. 3 (ed. J. S. Brown), 201-207.

Eck, R. V., Lippincott, E. R., Dayhoff, M. O. and Pratt, Y. T. (1966) Thermodynamic equilibrium and the inorganic origin of organic compounds, *Science 153*, 628-633.

Edwards, W., and Trotter, F. M. (1954) *The Pennines and Adjacent Areas*, Dept. of Scientific and Industrial Research, Geological Survey and Museum. London: Her Majesty's Stationery Office.

Ford, T. D. (1955) Blue John fluorspar, *Proc. of the Yorkshire Geol. Soc. 30*, No. 4.

_____ . (1967) Stratiform ore deposits of Derbyshire, in *Sedimentary Ores: Ancient and Modern* (Revised) Proceedings of the Dept. of Geology, Univ. of Leicester, 73-96.

Ford, T. D., and King, R. J. (1968) Mineralization in the Triassic rocks of south Derbyshire, *Trans. Inst. Min. Met. B77*, 42-43.

Flory, P. J. (1953) *Principles of Polymer Chemistry*. Ithaca, N.Y.: Cornell Univ. Press.

Friedman, N., Bovee, H. H., and Miller, S. L. (1970) High temperature pyrolysis of C_1 to C_4 hydrocarbons, *J. Org. Chem. 35*, 3230-3232.

Garnett, C. S. (1920) Colouring matters of red and blue fluorite, *J. Chem. Soc., 117*, pt. I, 620-622.

Giardini, A. A., Salotti, C. A., and Lakner, J. F. (1968) Synthesis of graphite and hydrocarbons by reaction between calcite and hydrogen, *Science 159*, 317-319.

Gelpi, E., Nooner, D. W., and Oro, J. (1970a) Isoprenoids and other hydrocarbons in terrestrial graphite, *Geochim. Cosmochim. Acta 33*, 959-972.

_____ . (1970b) The ubiquity of hydrocarbons in nature: aliphatic hydrocarbons in dust samples, *Geochim Cosmochim. Acta 34*, 421-425.

_____ . (1970) Organic compounds in meteorites—III. Distribution and identification of aliphatic hydrocarbons produced by open flow Fischer-Tropsch processes, *Geochim. Cosmochim. Acta 34*, 945-956.

Han, J., and Calvin, M. (1969) Occurrence of fatty acids and aliphatic hydrocarbons in a 3-4 billion year old sediment, *Nature 224*, 576-577.

Han, J., Simoneit, B. R., Burlingame, A. L., and Calvin, M. (1969) Organic Analysis on the Puebilto de Allende Meteorite, *Nature 222*, 364-365.

Hayes, J. M. (1968) Organic constituents of meteorites—a review, *Geochim. Cosmochim. Acta 31*, 1395-1440.

Hayatsu, R. (1966) Artifacts in polarimetry and optical activity in meteorites, *Science 153*, 859-869.

Heidberg, J., and Krejci-Graf K. (1969) Elaterite—a fossil polyethylene, *Naturwiss. 10*, 513-514.

Holland, H. D. (1962) Model for the evolution of the Earth's atmosphere, *Petrologic Studies:* a vol. to Honor A. F. Buddington, 447-477.

Hubbert, M. King (1953) Entrapment of petroleum under hydrodynamic conditions, *Bull. Am. Assoc. of Pet. Geologists 37*, 1954-2026.

Hunt, J. M., Stewart, F., and Dickey, P. A. (1954) Origin of hydrocarbons of Uinta Basin, Utah, *Bull. Amer. Assoc. of Pet. Geologists 38*, 1671-1698.

Irving, C. S., and Petterson, R. C. (1967) Formation of hydrocarbons in model primitive earth atmospheres, *Nature 32*, 3714-3715.

Kent, P. E. (1954) Oil occurrences in coal measures of England, *Bull. Amer. Assoc. of Pet. Geologists 38*, 1699-1713.

_____ . (1966) Oil, in *Nottingham and its Region*, British Assoc. for the Advancement of Science, 297-303.

King, L. H. (1963) Origin of the Albert mines oil shale and its associated Albertite, Dept. of Mines and Technical Surveys, Ottawa Research Report R 115.

King, R. J. (1959) The mineralization of the Mountsorrel Granodiorite, *Trans. Leic. Lit. Phil. Soc. 53*, 18-29.

Kvenvolden, K. A., and Hodgson, E. W. (1969) Evidence for porphyrins in early pre-cambrian Swaziland system sediments, *Geochim. Cosmochim. Acta 33*, 959-972.

Kvenvolden, K., Lawless, J., Pering, K., Peterson, E., Flores, J., Ponnamperuma, C., Kaplan, I. R., and Moore, C. (1970) Evidence for extraterrestrial amino acids and hydrocarbons in the Murchison Meteorite, *Nature 228*, 923-925.

Kvenvolden, K. A., Peterson, E., and Pollock, G. E. (1969) Optical configuration of amino acids in Precambrian Fig Tree chert, *Nature 221*, 141-143.

Kranz, R. L. (1968) Participation of organic compounds in the transport of ore metals in hydrothermal solution, *Inst. of Mining and Metallurgy*, B11, B26-B36.

Landa, S. and Machacek, V. (1933) Adamantane. a new hydrocarbon extracted from petroleum, *Coll. Czechoslav Chem. Communication 5*, 1-5.

Lasaga, A. C., and Holland, H. (1970) Chemical processes in the early atmosphere a further step towards understanding the origin of life, Princeton Univ. Chem. Dept. Junior paper.

Levorsen, A. I. (1956) *Geology of Petroleum*. San Francisco: W. H. Freeman and Co., 655.

Lister, M. (1673) On a subterraneous fungus, and a mineral juice, *Phil. Trans. 8*, 6179.

Love, J. D., and Good, J. M. (1970) Hydrocarbons in thermal areas of northwestern Wyoming, *Geol. Survey Prof. Paper 644-B*, B1-B23.

Lovely, H. R. (1946) Geological occurrence of oil in the United Kingdom with reference to present exploratory operations, *Bull. Amer. Assoc. of Petrol. Geologists 30*, 1444-1516.

Mahan, B. H. (1962) Vacuum ultraviolet photolysis of methane, *J. Chem. Phys. 37*, 207-211.

Magee, E. M. (1963) Photolysis of methane by vacuum-ultraviolet light, *J. Chem. Phys. 39*, 855-858.

McCarthy, E. D. (1967) PhD. Thesis, Organic Geochemistry, University of Calif. Lawrence Radiation Lab, 178.

McCarthy, E. D., and Calvin, M. (1967) Organic geochemical studies. I. Molecular criteria for hydrocarbon genesis, *Nature 216*, 642-647.

McKetta, J., Jr., (1962) High-temperature chemistry of the light hydrocarbons, *Adv. in Pet. Chem. and Refining 5*, New York: Interscience Pub., 378-412.

Meadows, A. J. (1970) Surface temperature of the early earth and the nature of the terrestrial atmosphere, *Nature 226*, 927-928.

Miller, S. L. (1953) A production of amino acids under possible primitive earth conditions, *Science 117*, 528-529.

Moorebath, S. (1962) Lead isotope abundance studies on mineral occurrences in the British Isles and their geological significance, *Phil. Trans. Roy. Soc. (A) 254*, 295-360.

Mueller, G. (1951) A genetical and geochemical survey of the Derbyshire mineral deposits, PhD. thesis. University of London.

_____ . (1954a) The theory of genesis of oil through hydrothermal alteration of coal type substances within certain lower Carboniferous strata of the British Isles, International Geological Congress, 19th Session, Algiers, No. 12, 279-328.

_____ . (1954b) The distribution of colored varieties of fluorite within the thermal zones of Derbyshire mineral deposits, International Geological Congress, 19th Session, Algiers, No. 13, 523-539.

_____ . (1954c) Enclosures in gangue minerals, *Mining. Mag.* (London) *90*, 148-150 and 208-217.

_____ . (1969) Discussion of evidences indicating the existence of petroleums of distinct genetical histories, Report 22nd Int. Geol. Cong. (Delhi) Part 1, 38-63.

_____ . (1970) Indications of High Temperature Processes in Organic Geochemistry, In *Advances in Organic Geochemistry* by G. D. Hobson and G. C. Speers, Pergamon Press, 443-467.

Munday, C., Pering, K., and Ponnamperuma, C. (1969) Synthesis of acyclic isoprenoids by the gamma irradiation of isoprene, *Nature 223*, 867.

Nakanishi, K. (1962) *Infrared Absorption Spectroscopy*. San Francisco: Holden-Day, Inc.

Noyes, W. A., Jr., and Leighton, P. A. (1941) *The Photochemistry of Gases*. New York: Dover Pub., Inc., 330.

Oro, J., and Han, J. (1966) High temperature synthesis of aromatic hydrocarbons from methane, *Science 153*, 1393-1395.

Oro, J., and Nooner, D. W. (1967) Aliphatic hydrocarbons in Precambrian rocks, *Nature 213*, 1082-1085.

Parkinson, D. (1957) Lower Carboniferous reefs of northern England, *Bull. Amer. Assoc. of Pet. Geologists 41*, 511-537.

_____ . (1953) The Carboniferous limestone of Treak Cliff, Derbyshire, with notes on the structure of the Castleton reef belt, *Proc. of the Geologists Assoc. 64*, part 4, 251-268.

Pering, K., and Ponnamperuma, C. (1969) Alicyclic hydrocarbons from an unusual deposit in Derbyshire, England—a study in possible diagenesis, *Geochim. Cosmochim. Acta 33*, 528-532.

_____ . (1971) Aromatic hydrocarbons in the Murchison meteorite, *Science*, in press.

Petersilie, I. A., and Sorensen, H. (1970) Hydrocarbon gases and bituminous substances in rocks from the Ilimaussaq Alkaline Instrusion South Greenland, Mineralogical and Geological Museum of the University of Copenhagen, Contributions to Mineralogy No. 74, 59-76.

Ponnamperuma, C. (1964) Chemical evolution and the origin of life, *Nature 201*, 337-340.

_____ . (1965) The search for extraterrestrial life, *Sci. Teacher 32*.

_____ . (1970) Chemical evolution and the origin of life, *New York State Journ. of Med. 70*, 1169-1175.

Ponnamperuma, C., and Pering, K. (1966) Possible abiogenic origin of some naturally occurring hydrocarbons, *Nature 209*, 979-982.

Ponnamperuma, C., and Woeller, F. (1964) Differences in the character of C_6 to C_9 hydrocarbons from gaseous methane in low-frequency electric discharges, *Nature 203*, 272-274.

Ponnamperuma, C., Woeller, F., Flores, J., Romiez, M., and Allen, W. V. (1969) Synthesis of organic compounds by the action of electric discharges in simulated primitive atmospheres. Amer. Chem. Soc. *Adv. in Chem. 80*, 280-288.

Pratt, W. R., and Rogers, R. G. (1961) Petroleum resources in basement rocks, *Bull. Amer. Assoc. Petrol. Geol. 45*, 397.

Ransome, F. L. (1921) The ore of the Almaden Mine, *Econ. Geol. 16*, 313-321.

Roedder, E. (1967) Fluid inclusions as samples of ore fluids, in *Geochemistry of Hydrothermal Ore Deposits* ed. by H. L. Barnes, New York: Rinehart and Winston, Inc., 515-574.

_____ . (1969) Environment of deposition of stratiform (Mississippi Valley Type) ore deposits for studies of inclusions, in *Genesis of Stratiform lead-zinc-barite-fluorite deposits, Mono. 3 of Econ. Geol.* J. S. Brown, ed., 349-362.

Rudakov, G. (1970) Transformations of subsurface petroleum, *Nature 225*, 370-371.

Sawkins, F. J. (1966) Ore genesis in the north Pennine orefield, in the light of fluid inclusion studies, *Econ. Geology 61*, 385-401.

Shirley, J., and Horsfield, E. L. (1940) The Carboniferous limestone of the Castleton-Bradwell area, North Derbyshire, *Quart. Journ. Geol. Soc. London 96*, 271-299.

Silverman, S. R., and Epstein, S. (1961) Carbon isotopic composition of petroleum and other sedimentary organic materials, *Bull. Amer. Soc. Petrol. Geol. 42*, 998-1012.

Simpson, I. M., and Broadhurst, F. M. (1969) A boulder bed at Treak Cliff, North Derbyshire, *Proc. York. Geol. Soc., 37*, 141-152.

Smith, J. W., Schopf, W., Kaplan, I. R. (1970) Extractable organic matter in Precambrian cherts, *Geochim. Cosmochim. Acta 34*, 659-676.

Studier, M. H., Hayatsu, R., and Anders, E. (1968) Origin of organic matter in early solar system I. Hydrocarbons, *Geochim.Cosmochim. Acta 32*, 151-173.

Suter, H. H. (1960) *The General and Economic Geology of Trinidad*, B. W. I., London: Her Majesty's Stationery Office.

Treibs, A. (1934) Organic minerals, III, Chlorophyll and hemin derivatives in bituminous rocks, petroleums, mineral waxes, and asphalts, Origin of petroleum, *Ann. 510, 42*.

Welte, D. H. (1965) Relation between petroleum and source rock, *Bull. Amer. Assoc. of Pet. Geologists 49*, 2246-2268.

Winters, J. C., and Williams, J. A. (1969) Microbiological alteration of crude oil in the reservoir, *Preprints—Div. of Petroleum Chemistry, ACS 14*, E22-E31.

Wolfendon, E. B. (1958) Paleoecology of the Carboniferous reef complex and shelf limestones in Northwest Derbyshire, England, *Bull. Geol. Soc. of America 69*, 871-898.

Wood, J. A. (1968) *Meteorites and the Origin of Planets*. New York: McGraw-Hill Book Co.

Yates, R. G., and Thompson, G. A. (1959) Geology and Quicksilver Deposits of the Terlingua District, Texas. *U.S. Geol. Surv. Prof. Paper 312*, 1-114.