CHAPTER 8

NATIVE BITUMENS ASSOCIATED WITH OIL SHALES*

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Introduction

A variety of native bitumens are present among the organic constituents of oil shales. These substances range from liquid petroleum through heavy, viscous "tars" and "asphalts" to solid asphaltites and asphaltic pyrobitumens. The deposits exist in many forms. Petroleum occupies the porous parts of adjacent strata and may even be found in pores and fractures within the oil shales. Semi-liquid "tars" and "asphalts" occur in the same manner as petroleum and in some places seep from pores or fractures of outcrops. The solid substances may occur as blebs, nodules, stringers, and veinlets in the oil shales and adjacent rocks, and as veins, some of which are of tremendous size, that cross-cut the oil shales and adjacent rocks.

The organic material that was deposited as an original constituent of oil shales generally is considered to be the source of the bitumens associated with these rocks. Until recently there has been but little investigation of the composition and chemistry of these bitumens. The following discussion is a summary of recent studies of the geology and chemistry of some of these substances found on the North American continent. The discussion is intended to be general, but because the bitumen deposits associated with the Green River Formation in the Uinta Basin of northeastern Utah have been studied in considerable detail, they are described as type examples.

Oil Shales

Oil shales occur throughout the geologic column from the Cambrian through the Tertiary systems, and undoubtedly some were deposited wiring the Precambrian, beginning at the time when algae and other primeval forms of life became abundant. The earliest formed oil shales have not been preserved as such, generally having been subjected to...
considerable metamorphism, and now appear as graphitic shales, slater. and schists. Oil shales are forming now where muds and marls rich in organic matter are being deposited under anaerobic conditions. The term "oil shale" is used loosely to designate rocks that yield liquid hydrocarbons by pyrolysis. No precise definition that adequately includes all rocks that are commonly called "oil shales" has been composed, and it is not considered practical to attempt to do so now. A small part of the organic matter present in oil shales, from 1 to 5% of the total can be extracted with carbon disulfide, carbon tetrachloride, and other organic solvents. The bulk of the organic material is insoluble and can be made to yield hydrocarbons, or "oil", only by the application of heat. The yield of oil shales ranges from a small amount to approximately 1 gal of oil per ton of rock for some exceptionally rich material. Quite commonly a utilitarian limit is applied to the term, and rocks that yield less than 10 gal of oil per ton are not considered to be oil shales.

Many rocks that are called "oil shales" are not shales at all. For example, most of the so-called rich "oil shale" beds of the Green River and Uinta Basins consist predominantly of chemically precipitated carbonate minerals and are marlstones. Some of the rich beds of the Albert Shales of New Brunswick, Canada, also consist mainly of carbonate minerals. The oil shales are members of gradational rock series in which the end members are on the one hand clay shales or marlstones, and on the other are cannel coals or torbanites. They are similar in the respect that all contain significant quantities of waxy and resinous organic material that can be extracted with carbon disulfide, carbon tetrachloride, and other organic solvents. The bulk of the organic material is insoluble and can be pyrolysed as a means of extracting hydrocarbons from these substances. As discussed in Chapter 5, the nature and composition of kerogen varies from one oil shale to another; consequently, a variety of bitumens are produced from different oil shales.

Characteristics of Some Oil Shale Bitumens

The principal physical properties and some of the chemical characteristics of the most abundant oil shale bitumens are presented in Table 1. The chemical properties and compositions of these substances are discussed in a following section.

These data indicate the approximate ranges of the physical properties and ultimate compositions of the oil shale bitumens. Inasmuch as these substances are not completely uniform from one deposit to another, or even within the same deposit, minor deviations from these values are not uncommon.

Bitumen Deposits

The substances described in this paper are intimately associated with oil shales, that is, they are found within the oil shales or the adjacent rocks and their obvious origin is from the organic matter in the oil shales. These bitumens include albertite, gilsonite, wurtzilite, some anthraxolites, some asphaltic bitumens, and other related substances. Other bitumens,

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**Table 1: Characteristics of Some Oil Shale Bitumens**

| Bitumen | Characteristic | Value
|---------|----------------|-------
| Bitumen 1 | Ultimate Composition | 111.2
| Bitumen 2 | Ultimate Composition | 111.2
| Bitumen 3 | Ultimate Composition | 111.2

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**Note:** The table continues with similar entries for other bitumens.
such as grahamite, glance pitch, and manjak, are not included because they are generally considered to be residues of inspissated petroleum, the deposits are not associated with oil shales.

Albert County, New Brunswick, Canada—The Albert shale formation of Lower Carboniferous age that crop out in the southern part of New Brunswick include rich oil shale beds. These shales have been described by Bailey and Ells (1878) as follows:

"The bulk of the formation consists of shales, but while these prevail in the group, numerous beds of fine-grained sandstone, greater or less thickness; and occasionally, but rarely, thin beds of conglomerate. The shales are, in general, thinly bedded, and often papyraceous, splitting easily into thin and flexible sheets, but alternate with these are thicker and harder beds, destitute of any lamination, tough, and breaking only with a conchoidal fracture. Both the sandstones, in common with the other Lower Carboniferous rocks of the district, are highly calcareous, so much so, indeed, that, at times to approach a true limestone in character, while both calcareous and ferruginous bands and nodules are of frequent occurrence. The peculiar feature, however, of the group, as well as the most persistent to the extent to which they are everywhere impregnated with bituminous matter."

The above description indicates that the Albert Shale Formation is quite similar to the lacustrine facies of the Green River and Uinta Formations of the Uinta Basin. Much of the "oil shale" of both localities is marlstone. Some of the highly kerogenous Albert Shale has a characteristic odor similar to that of the oil shales in the Uinta Formation.

Several veins of an asphaltic pyrobitumen cross-cut the shales in the vicinity of Hillsborough and Albert Mines. Many thousands of tons of this material were mined during the period from about 1850 to 1880 and used mainly in the manufacture of illuminating gas. It originally was called "albert coal" and later "albertite". The largest known vein, located about 2 miles north of Albert Mines, followed the axis of an anticline. This vein was irregular in form, was nearly vertical, averaged several feet in width, and was mined out to a depth of about 1300 ft over a distance of nearly three-quarters of a mile along the strike. The vein material evidently has been metamorphosed to slate because it now has, on an ash-free basis, a high carbon content, about 95%, and only about 2-5% volatile matter. The original organic deposit evidently has been metamorphosed into enclosing slates because it now has, on an ash-free basis, a high carbon content, about 95%, and only about 2-5% volatile matter. The vein material was fractured and considerable amounts of quartz and sulfur minerals were deposited in the openings.

Describing the Sudbury deposits Coleman (1928) states, "The general character of the vein material cannot be determined precisely, but the substance could have been similar to the New Brunswick albertite one of the pyrobitumens of the Uinta Basin.

Basin, Utah—The Uinta basin of northeastern Utah (Fig. 1) is for many deposits of native bitumens that occur in lacustrine and jarnbrian Onwatlin Slate of the Sudbury District have been described by Coleman (1897, 1928) and Mickle (1897), and similar veins in the Precambrian Gunflint Formation of the Thunder Bay have been described by Tanton (1931) and Chapman (1865). The occurrences have been investigated quite thoroughly. The largest vein, having a maximum width of about 9 ft, is irregular in form, vertical, and cuts across the stratification of the metamorphosed shale. The original organic deposit evidently has been metamorphosed into enclosing slates because it now has, on an ash-free basis, a high carbon content, about 95%, and only about 2-5% volatile matter. The vein was fractured and considerable amounts of quartz and sulfur minerals were deposited in the openings. The only "oil shale" of both localities is marlstone. Some of the highly kerogenous Albert Shale has a characteristic odor similar to that of the oil shales in the Uinta Formation.

FIG. 1. Map of Uinta Basin.
fluvialite sedimentary rocks of early Tertiary age. The Uinta Basin, structural, topographic, and sedimentary basin that was formed during the Cretaceous-Eocene transition period. During the Eocene epoch it was the site of large Lake Uinta in which was deposited a thick sequence of marlstones, and limestones that includes many oil shale units. Most bitumens that occur within the basin are derived from these oil shale units.

The Late Cretaceous and Tertiary stratigraphic section of the Uinta Basin consists of the following formations:

**Tertiary:**
- **Oligocene:** Duchesne River Formation—predominately sandstone and conglomerate.
- **Eocene:** Uinta Formation—consists of a fluvialite sandstone facies and a lacustrine shale-marlstone-limestone facies.
- Green River Formation—includes alluvial, deltaic, and lacustrine facies.
- Wasatch Group—includes marine, fluvialite, lacustrine, and alluvial sediments, some coal beds.

**Mesozoic:**
- **Upper Cretaceous:**
  - Mesa Verde Group—includes marine and fluvialite shales and sandstones, and a large amount of coal.
  - Mancos Shale—marine shale with minor impure limestone.

During a part of the Late Cretaceous epoch the site of the Uinta Basin was a shallow seaway in which there were deposited the marine Mancos Shale and basal beds of the Mesa Verde Group. Near the close of the Late Cretaceous epoch the sea became shallower, and after some minor regressions and transgressions withdrew entirely from the area. This interval is represented by fluvialite shales and sandstones interspersed with minor marine beds of the Mesa Verde and Wasatch Groups. A thickness of six thousand feet of sediments was deposited, and these beds now crop around the periphery of the basin.

Near the close of the Late Cretaceous epoch, or very early in the Eocene epoch, the Uinta Basin began to form, and the sedimentary environment changed to predominately lacustrine conditions. Several hundred feet of sandstones, shales, and mudstones of the middle and upper parts of the Wasatch Group were deposited around the margins of the basin while the deeper parts of the basin were cut off and started to have abnormal salinity! Lake Uinta thus came into existence and lasted until about the beginning of the Oligocene epoch. During the life of the lake, sedimentation within the basin consisted of a lacustrine facies in the center surrounded by shore-line or deltaic facies, and locally fluvialite and alluvial facies around the edges. These facies are present in the Wasatch Group and throughout the Green River and Uinta Formations. During the early part of the Oligocene epoch the alluvial Duchesne River Formation was deposited in the northern part of the basin.

The term “Wasatch” usually has been used to designate the fluvialite sandstone facies of the basin sediments and the term “Green River” to designate the lacustrine facies. Recent usage of the terms Wasatch and Green River has come to denote time-stratigraphic intervals. The deposition of lacustrine, shore-line, fluvialite, and alluvial sediments was continuous through the entire Eocene epoch although there was considerable fluctuation of the level of deposition and size of areas covered. The boundaries between the Wasatch-Green River and Green River-Uinta sediments are in part arbitrarily fixed.

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A generalized section across the Uinta Basin is shown by Fig. 2. Source beds of the various kinds of bitumens are indicated within the appropriate stratigraphic intervals.

The lacustrine beds of the basin sediments are of particular interest to this discussion because they include the "oil shale" source beds of the bitumens. They consist of a sequence of interbedded paper shales and marlstones interspersed with a few sandstones, mudstones, and limestones having a total thickness of over 4000 feet. Moreover, they extend without depositional gaps from the upper part of the Wasatch Group through the entire Green River and Uinta Formations. The lacustrine beds interfinger with fluvialite sandstones and locally are overlapped by great thicknesses of them. The presence of saline minerals, predominately sulfates and carbonates, or of casts formed by crystals of these minerals, indicate that the lake waters reached a high degree of salinity. The saline constituents were mostly sulfates, carbonates, and bicarbonates and apparently included only minor quantities of chlorides. In general the salinity increased with the age of the lake. The waters, at least intermittently, were stratified.

(pic. 2. Generalized section of the Uinta Basin before deformation and erosion.)
with the surface layer being aerated and supporting abundant life, the bottom layer being stagnant and sulfurous. "Oil shales" are irreducible distributed throughout the lacustrine facies. These rocks are predominately marlstones consisting of more than 50% of carbonate minerals. The thickness varies from a few inches to several feet in thickness and tends to occur in groups. Some of the thickest and richest oil shale groups occur near the base of the Green River Formation in the vicinity of Soldier Summit, the Parachute Creek Member of the middle part of the Green River Formation that extends almost throughout the entire basin, and in the Uinta Formation in the vicinity of Indian Canyon.

More complete descriptions of the stratigraphy of the Uinta basin are presented in the following references; for the Wasatch Group, Spieker and Eldridge (1925), Spieker (1946); for the Green River Formation, Brao (1931); for the Uinta Formation, Dane (1954); and for the Duchesne River Formation, Peterson and Kay (1931) and Kay (1934).

Petroleum. Petroleum occurs in stratigraphic traps in sandstones near the base of the Green River Formation at several places along the north margin of the Uinta Basin. Crude oils recovered from the Red Willow, Roosevelt, Duchesne, County, and Flat Mesa pools are highly paraffinic with little to essentially no asphaltic constituents. Their colors range from a medium green to very pale yellow, specific gravities range from 28° to 41° API, and pour points range from about 68° to 92°F because of the low amount of paraffin wax they contain. The source beds of this oil are lacustrine sediments of Wasatch and lower Green River age. Oil from shallower Green River horizon at Duchesne is different, being asphaltic instead of paraffinic and resembling gilsonite chemically.

Shows of black, asphaltic petroleum have been found in sandstone strata of the lower and middle parts of the Green River Formation. This petroleum probably originated in oil shales or other lacustrine beds of the Green River Formation. It undoubtedly migrated from the oil shales into the fluvialite sandstones around the margin of the basin and became partially inspissated, thereby forming the rock asphalt deposits.

Ozocerite. Near Soldier Summit, at the southwest edge of the basin, the native mineral wax, ozocerite, occurs in fracture zones in soft shales and sandstones of the Wasatch Group. Within the fracture zones, which range up to about 30 ft in width, the ozocerite forms films on the brecciated rock and irregular veins and nodules. Reports of former mining operations indicate that ozocerite may comprise as much as 30% of the material in the fracture zones, but generally the amount is much smaller. The deposits are in Wasatch beds which are stratigraphically below the oil shales on the outcrop. The ozocerite appears to be closely related chemically to the crude oil produced at Roosevelt and Duchesne from lower horizons of the Green River facies.

Rock asphalt. Some of the largest deposits of bituminous sandstone in the United States are found along the borders of the Uinta Basin where the upturned Tertiary fluvialite sandstones are exposed or where erosion developed deep canyons and cliff faces in them. Other deposits occur in places within the basin, some of which are in limestone or marl beds. The most of the bitumen occurs in strata of the lower and middle of the Green River Formation, but locally some of it has migrated stratigraphically lower and higher formations and even into the tie of recent alluvium. The largest known deposits are located in the Uinta Cliffs near Sunnyside and F.R. Springs, in Asphalt Ridge near Kfnai, and along Raven Ridge and the west side of Grand Hogback on the j-th eastern margin of the basin.

"Infrared spectra of the organic matter extracted from sandstones in the Uinta Basin are mostly similar to spectra of gilsonites, and for a few samples are similar to spectra of wurtzilites. It appears most likely that the bitumen Originated in lacustrine beds of the Green River Formation, especially the oil shales. The source beds cannot be determined definitely, but they probably are in the middle or lower part of the formation below the source beds of gilsonite and above those of albertite. The bitumen has migrated laterally into permeable sands of the same age in the central and southern parts of the basin. The rock asphalts along the north side of the basin, including those at Asphalt Ridge, were formed by bitumen migrating along unconformity surfaces where the source beds are truncated by a series of post-Green River pre-Duchesne River unconformities.

Albertite. A pyrobitumen that has physical and chemical properties similar to the albertite of New Brunswick occurs in veins in lacustrine beds of the lower part of the Green River Formation near the southwest margin of the Uinta Basin. While it is unlikely that these two substances are precisely identical in composition, the resemblance is close enough that it is convenient to call the Uinta Basin material albertite also.

The Uinta Basin albertite occurs in veins within platy marlstones lying about 600 ft above the base of the Green River Formation. The veins mostly are narrow stringers from a fraction of an inch to a few inches in width and a few yards in length; but one vein (originally called nigrite by Eldridge, 1901) is at least 300 ft long, has a maximum width of about 2 ft, and has been prospected to a depth of about 30 ft. The vertical dimensions of the veins are controlled by the thicknesses of the platy marlstone strata because the veins pinch out in adjacent shaly beds. Within the veins the albertite is essentially free from wall rock fragments and other visible mineral matter. The albertite does not penetrate the wall rock but does fill small side fractures. Some of the wall rock strata contain lenses of organic matter, other strata are devoid of visually recognizable organic matter.

The source of the albertite undoubtedly is in "oil shale" beds within the platy marlstones. There is no evidence that the bitumen migrated through shaly strata separating the marlstones. The known distribution of albertite is restricted to the Soldier Summit locality.

Ingramite. Ingramite is a solid pyrobitumen occurring in lacustrine beds about 300 ft above the base of the Green River Formation in the Soldier...
Summit locality. The substance is very similar to albertite and probably the Utah-Colorado state line, and in the Myton-Fort Duchesne strict about 40 miles to the west.

The gilsonite veins range from small deposits an inch or so in width and 18 ft. in length to large deposits several feet in width and several miles 1Pth of about 900 ft. The Rainbow Vein in the Rainbow Group has a minimum width of 10 ft, an outcrop length of about 16 miles, and has been mined through a vertical distance of several hundred feet. The Cowboy Vein is the largest deposit. There are many smaller veins.

Veins

The gilsonite veins are remarkable for their nearly uniform features. They are nearly straight, extending across the country in lines almost as if seeded out by transit. The walls are surprisingly smooth and do not deviate from the vertical by more than about 5°. In mining operations the gilsonite breaks clean from the walls leaving smooth sandstone faces. The vein material generally is pure bitumen. Horses and fragments of wall rock occasionally occur in some veins and apparently do not occur in others. Some horses have been found suspended in the gilsonite only a few feet from the places where they were broken from the walls.

Most of the known gilsonite veins occur in massive sandstones of the Uinta Basin. Some of them increase slightly in width with depth and others maintain a nearly uniform width. Near the base of the sandstones the veins become narrower and then feather out into a large number of veinlets, stringers, and nodules in the shales and marlstones of the upper part of the Green River Formation. The "veinlets" or "roots" can be traced downward until finally they reach the apparent source of gilsonite in the rich oil shales of the Parachute Creek member of the Green River Formation. The feathering out of large gilsonite veins into Green River Shales can be observed where veins of the Bonanza Group are exposed on the north wall of the White River Canyon and where the Rainbow Vein crosses some of the canyons tributary to Evacuation Creek. In some localities the dispersed veinlets pass through the oil shales, then coalesce to form large gilsonite veins in massive sandstones at the base of the Green River Formation and in the upper part of the Wasatch Group.

The Rainbow Vein system is an excellent example of the existence of gilsonite both above and below its apparent source in the oil shales. The northwest end of the vein crops out in massive sandstones of the Uinta Formation. This section of the vein has been mined over a distance of several miles with the workings extending downward to where the main vein branches into the Green River Shales. Toward the southeast the vein outcrop branches into successively lower units of the stratigraphic section. The middle part of the outcrop is in oil shales and paper shales of the Green River Formation and appears as a large number of narrow veinlets and stringers. There must be some continuity of veinlets through the shales although most of those appearing on the outcrops terminate upwards,
downwards, or both, within the shales. For a distance of about 3 miles near the southeast end of the vein its outcrop is in massive sandstones near the base of the Green River Formation. The southeast end of the vein is in the Wasatch Group. The portal of the abandoned Dragon mine is in sandstone near the base of the Green River Formation. This mine was worked to a depth of at least two hundred feet and apparently below the base of the Green River Formation. The vein terminates downwards in clays and mudstones of the Wasatch Group.

The Weaver-Colorado Vein that is southeast of the Bonanza Group, and which may be an extension of the Wagon Hound Vein of that group, has an outcrop about seven miles long. Almost all of this length is in lower Green River and upper Wasatch strata and below the apparent oil shale source beds.

The Rainbow and Weaver-Colorado gilsonite veins are the only ones that have been eroded to such depths that their basal sections below the oil shales are exposed. The outcrops of all other known veins are in Upper Green River, Uinta, or Duchesne River strata. There has been no exploration of these veins by mining or drilling below the Green River Shales, therefore, it is not known whether or not they have extensions below the oil shales. The presence of massive sandstones below the oil shales is favorable for the existence of large veins while the presence of clays and shales is unfavorable.

There has been considerable controversy concerning the origin of the fissures occupied by the gilsonite. There has been essentially no displacement of strata, either vertically or horizontally, along these fissures. In the mined out parts of the veins stratification features can be followed along both walls with no indication of displacement. The most reasonable explanation appears to be that the fissures are large tension cracks formed during down-warping of the basin following deposition of the Green River and Uinta sediments.

Gilsonite commonly has not penetrated the wall rocks except along those parts of the veins close to the oil shales, and below them. Reports differed considerably on this matter, some observers having claimed that gilsonite-saturated rock wall is the prevalent condition, while others have stated it to be the exception. The viewpoints probably depend upon what parts of the veins were examined. Along those parts of the veins that are about four or five hundred feet or less above the source beds in the oil shales, gilsonite has commonly penetrated the wall rocks; thus along part of the Rainbow Vein system in the Uinta Sandstone the wall rock in many places is saturated with gilsonite to distances of several feet from the vein. Gilsonite also has penetrated the sandstone along the walls of minor fractures, some of which extend a few hundred feet from known major veins. Along the south eastern part of the Rainbow Vein system that is in the lower Green River and Wasatch Sandstones most of the wall rock has been penetrated by the gilsonite. The same condition exists along the part of the Weaver-Colorado Vein that is in lower Green River Sandstone. Gilsonite has penetrated the

The physical and chemical characteristics of gilsonite are variable from one part of a vein to another and from vein to vein. In general, the gilsonite I occurs as a solid homogeneous mass that breaks with a conchoidal fracture. In the marginal parts of some veins it has a fine columnar structure perpendicular to the walls. This gilsonite is called "pencilled ore" and may occur on one or both walls of a vein. The homogeneous gilsonite in the interior of a vein generally has a lower fusing point, slightly lower specific gravity, higher solubility in organic solvents, and more lustrous appearance than the material close to the walls. For commercial purposes, gilsonite from the interior of the vein is classified as "selects" and that from the margins as "seconds". The proportions of "selects" and "seconds" vary between different veins and different parts of the same vein. Some of the narrower veins consist only of "seconds", and gilsonite near the outcrops almost all of the veins may be entirely "seconds". It is possible that some kind of weathering action may be responsible for the difference. Gilsonite in thin veins, along the walls of thick veins, and at the outcrops may have become slightly more polymerized than that in the interior of thick veins, or it possibly may have taken up oxygen to become slightly oxidized.

Plastic and liquid phases of gilsonite occasionally are found in some of the deeper mines such as those in the Tabor Vein of the Bonanza Group and the Castle Peak Mine near Myton. In some places these soft varieties of gilsonite are found within the veins and in some places they seep from fractures and porous parts of the wall rock. "Liquid gilsonite" was found at a depth of about 1900 ft in well No. 1 Jensen located in W 1/2 NE 1/4 sec. 1 T. 8 S., R. 16 E., Salt Lake Meridian.

Tabbyite. Tabbyite is a bitumen occurring in veins along Tabby Canyon. This locality is between the gilsonite and wurtzilite areas. The veins range from small stringers to deposits from which several tons of material have been mined. The tabbyite veins occur in lacustrine beds near the top of the Green River Formation, and the source of the bitumen appears to be in oil shale beds of this part of the section.

Wurtzilite. The pyrobitumen wurtzilite occurs in veins in an oil shale zone of the lacustrine facies of the Uinta Formation. The wurtzilite deposits appear to be restricted to a stratigraphic interval of about 50 ft and are located in the area including Indian, Lake, and Sams Canyons in the western part of the Uinta Basin.

The oil shales containing the wurtzilite were deposited near the end of the life of Lake Uinta when it had become greatly reduced in size and its
waters were highly saline and apparently were strongly sulfurous in the gilsonite area are known to extend from the upper part of the deeper parts. These "oil shales" are hard, tough, marlstones with sensuous beds through the Green River and Uinta Formations and into the conchoidal fracture and little tendency to split along bedding planes. The strata above and below the oil shales are much softer and consist of thjessel massive, thick-bedded sandstones, presumably under tensional strata and sandy shales that part readily along bedding planes. The sizes of the wurtzilite veins have been closely controlled by the enclosing strata. The wall rock oil shales are also the source beds of the veins. These hard marlstones are characterized by joints cross-cutting the stratification and few fractures along bedding planes. Open, nearly vertical fissures, are therefore, common. The adjacent shaly strata at* characterized by bedding plane fracture, therefore, the open fissures* within the marlstones terminate abruptly near the shale contacts. The vertical dimensions of the wurtzilite veins are limited to the thickness of the marlstones and generally are in the range of from 15 to 30 ft. The veins range from a fraction of an inch to a maximum of about 2 ft in width, and from a few feet to several thousand feet in length. The largest known ve

Some of the wurtzilite veins are branched, have off-sets, and are quite irregular in form. This condition results from a local block-like fracture pattern in the marlstone. Quite unlike gilsonite, wurtzilite has a tendency to cling to the wall rock and does not break "clean". This property resulted in considerable waste in mining because the wurtzilite could not readily be separated from the rock.

Although some of the wurtzilite veins are large, possible variations in the properties of the pyrobitumen are not apparent by visual examination. Wurtzilite occurs as an apparently homogeneous mass having conchoidal fracture, and generally is free from included wall rock fragments. Near the north edge of the wurtzilite area a semi-plastic bitumen seeps from fractures in the oil shale zone. This substance, sometimes called "liverite", has essentially the same chemical properties as wurtzilite and is considered to be a fluid phase of it.

Fracture control of the bitumen deposits. The solid bitumens of the Uinta Basin apparently have been squeezed into fissures, probably by the compaction of the sediments. The size and complexity of the fissures were determined partly by the physical characteristics of the rock that was ruptured and partly by their location with respect to the synclinal axis of the basin. In general, large, simple fissures developed in the massive, thick-bedded sandstones and marlstones, and small, irregular fracture systems developed in the thin-bedded shales and clays. The larger fissures were developed closest to the synclinal axis and roughly parallel to it.

The major fractures of the Uinta Basin were formed as the area was warped following deposition of the Green River and most of the Uinta sediments. The large fissures occupied by the gilsonite and wurtzilite veins, and possibly the smaller fissures occupied by tabbyite and albertite veins, are generally considered to be tension cracks. Some of the fracture systems now occupied by the gilsonite veins, extend from the bottom to the surface of the sandstone strata. In the Uinta Formation this distance exceeds a few hundred feet. In the basal sandstones of the Green River Formation it may reach up to about 400 ft. The great fissures in the sandstones, upon passing through the thin-bedded, fine-grained sediments, quickly split into a myriad of smaller fractures, most of which are vertical or nearly so, but some of which follow bedding planes. The fracture zones terminate both upwards and downwards in soft clays and mudstones. The large, gilsonite-filled fractures do not persist for more than a few tens of feet after passing from the sandstones. The outcrop of the Cowboy Vein of the Bonanza Group has a length of nearly 3 miles.

Some of the wurtzilite veins are branched, have off-sets, and are quite irregular in form. This condition results from a local block-like fracture pattern in the marlstone. Quite unlike gilsonite, wurtzilite has a tendency to cling to the wall rock and does not break "clean". This property resulted in considerable waste in mining because the wurtzilite could not readily be separated from the rock.

Although some of the wurtzilite veins are large, possible variations in the properties of the pyrobitumen are not apparent by visual examination. Wurtzilite occurs as an apparently homogeneous mass having conchoidal fracture, and generally is free from included wall rock fragments. Near the north edge of the wurtzilite area a semi-plastic bitumen seeps from fractures in the oil shale zone. This substance, sometimes called "liverite", has essentially the same chemical properties as wurtzilite and is considered to be a fluid phase of it.

Fracture control of the bitumen deposits. The solid bitumens of the Uinta Basin apparently have been squeezed into fissures, probably by the compaction of the sediments. The size and complexity of the fissures were determined partly by the physical characteristics of the rock that was ruptured and partly by their location with respect to the synclinal axis of the basin. In general, large, simple fissures developed in the massive, thick-bedded sandstones and marlstones, and small, irregular fracture systems developed in the thin-bedded shales and clays. The larger fissures were developed closest to the synclinal axis and roughly parallel to it.

The major fractures of the Uinta Basin were formed as the area was warped following deposition of the Green River and most of the Uinta sediments. The large fissures occupied by the gilsonite and wurtzilite veins, and possibly the smaller fissures occupied by tabbyite and albertite veins, are generally considered to be tension cracks. Some of the fracture
and others (1954) have shown that the soluble organic material extract! from the various source beds has the same composition, as indicated by infrared analyses and refractive indices, as the bitumens in associate fractures and saturated sands. These facts indicate that the composit** of the organic source material in different stratigraphic intervals wagi major factor in determining the kind of bitumen that separated from them. Highly paraffinic oil and ozocerite, which appear to have the same source 1 occur in beds of Wasatch age around the margins or in oil shale beds p<;sumably of the same age in the center. Known deposits of albertite and ingramite are very local in their occurrence and are associated with eij shale beds in the lower part of the Green River Formation. The source beds of gilsonite and tabbyite are the rich oil shales of the middle part of the Green River Formation. The bituminous sandstones, for the most pao» belong to fluviatile and shore-line facies of the Green River Formation that interfere with the lacustrine facies and its rich oil shales. *pull stratigraphic interval of the bituminous sandstones is above that of abenit and overlaps the lower part of the gilsonite interval. The infrared specific of organic extracts from the bituminous sandstones generally are similar[, that of gilsonite, but a few of them resemble wurtzilite (Hunt et al., 1955).

The source beds and stratigraphic interval of the wurtzilite are the oil shales near the top of the lacustrine section in the Uinta Formation.

The two factors that most influenced the composition of the organic constituents of the oil shales were the salinity and toxicity of the Uint Lake water. During early Tertiary time the climate of the area was warm and humid, and a temperate to semi-tropical fauna and flora flourished (Bradley, 1931; Berry, 1925). Initially, during Wasatch time, the lake water was fresh and aerated throughout, this being a condition that permitted large numbers of benthonic organisms to thrive. Near the beginning of Green River time the basin became permanently closed and then the lake water became increasingly saline. This condition is indicated by the deposition of calcitic limestone in the basal sediments (Wasatch), followed by chert, calcite, and dolomite (lower Green River), calcite, dolomite, and nahcolite (middle and upper Green River), and finally dolomite and highly soluble alkalai-alkaline earth carbonates in the uppermost sediments (Uinta). During early Green River time the lake became chemically stratified, at first intermittently, and then permanently, with the upper layer being aerated and supporting abundant life while the bottom layer was stagnant and sulfurous. This condition is indicated by the disappearance of benthonic fossils and by the presence of abundant sulfide minerals. A certain beds. The concurrent increase in salinity and toxicity was subject to many fluctuations but generally was continuous from the closing of the basin to the end of life of Lake Uinta.

As the salinity and toxicity of the lake water increased, the character of the bitumens changed. Thus, ozocerite consists mainly of paraffin hydro carbons and contains only traces of nitrogen and sulfur. Albertite, whi"l iated with sediments deposited in a very mildly saline environment, mainly of aromatic ring compounds and contains only slightly nitrogen and sulfur than ozocerite. Gilsonite, the source beds of which were deposited in a rather strongly saline environment, is presenantly aromatic and naphthenic and contains up to about 2% each nitrogen and sulfur. Wurtzilite, derived from source beds deposited in a highly saline and toxic environment, is naphthenic in character and a high sulfur content that ranges up to about 7%, but it has less nitrogen than gilsonite.

The aquatic life that flourished in Lake Uinta changed, both as regards species and relative abundance of various species, as salinity of the water increased. Fossil evidence of this condition shows a transition from a varied fucila d nora i bron ding an abundance of macrofossils in the basal lacustrine beds to an assemblage of lower orders of life represented mainly by microfossils in the middle and upper lacustrine beds. Fossil fossils are found in certain marginal facies. The oil shales themselves are equally barren of any higher forms of life. That the composition of organic matter in successively younger oil shales changed simultaneously with the salinity and the fauna and flora of the lake is indicated by the composition of soluble material that can be extracted from them. It is probable that the character of the bitumens is dependent in part upon the kinds of life that furnished the source organic material and in part upon the action of great constituents in the water in preserving this material.

The process by which both solid and viscous semifluid bitumens associated with oil shales were formed from indigenous organic matter is unknown. The many geologists who have examined the bitumen deposits associated with the Uinta Basin oil shales are in general agreement that these substances moved into the fissures, cavities, and porous rocks while in a fluid, although viscous condition. The fluids might have been essentially syngenetic constituents of the sediments, or they might have been formed from the organic matter by some chemical process. These observations apply equally well to the Albert Shale and the associated libertite.

Although oil shales and kerogen-rich rocks exist in many parts of the World, solid bitumens are associated with only a few of them. The oil shale formations that are source beds for the solid bitumens have, in common, some significant characteristics: (1) they include thick strata having exceptionally high organic contents and may yield on retorting from about 40 to as much as 100 gallons of oil per ton of rock; (2) they have been buried under several thousand feet of cover; (3) they have been folded during the course of regional deformation; (4) large fissures developed in the oil shales and adjacent rocks during the folding; (5) they have been subjected to considerable compaction, both from the weight of overlying sediments and from pressures developed during folding. On the other hand, oil shales that have not been source beds for solid bitumens generally have these characteristics: (1) their content of organic matter is relatively...
low, but there are some exceptionally rich oil shales in this group; (3) they have been buried under thin covers of sediments ranging from a few tens to a few hundreds of feet thickness; (3) they have not been folded and lie nearly horizontally or with slight regional dips; (4) they have not been subjected to appreciable compaction.

The features enumerated above may explain why many oil shale formations, such as the Chattanooga and its correlatives in the United States and the Cambrian-Ordovician shales of the Baltic region of Europe have not given rise to deposits of solid bitumens. The Chattanooga is a "lean" oil shale in comparison with the Green River and Albert Shales and it has not been folded. The Cambrian-Ordovician Shales of the Baltic region include some rich oil shale strata, but these formations lie nearly horizontal, have never been buried under a thick cover, and have not been subjected to profound compaction. The Dictyonema and Kukersite Shales of the eastern Baltic region apparently have given rise to no solid bitumens, at least the authors have found no reference to such substances in the available literature. In the Billingen-Mosseberg area, Vastegotland, Sweden, small veins of a bitumen having the physical characteristics of gilsonite occur in oil shale and blue clay at a depth of about 100 m below a thick diabase sill (Dr. T. Bertil Dahlman, Geological Survey of Sweden, oral communication). The oil shale in this locality is very "lean", and it is thought that much of the original organic matter was distilled out by heat from the igneous intrusion, and that the veins of bitumen were formed at the same time. Bitumen veins are not known to be associated with oil shales in other areas of Sweden.

There is no evidence of former thermal activity in the Uinta Basin and in the vicinity of the Albert Shales that can be attributed to igneous intrusions. Temperatures that have existed within these oil shales have been determined by the geothermal gradient and depth of burial. Within the Uinta Basin a rough estimate places the maximum temperature that existed in the albrite zone, buried at a depth of about 6000 ft, at about 140°F, and in the wurtzilite zone, buried at a depth of about 2000 ft, at about 90°F. Maximum temperatures that have existed within the Albert Shales probably fall within this range. These temperatures are insignificant as a cause of pyrolysis; therefore, this process can be eliminated as playing any significant role in the genesis of the bitumens.

The authors believe that the mechanism by which the bitumen deposits moved from their shale source beds into the fissures was probably viscous flow under the differential pressure set up by the opening of the fissures. The fluids must have been viscous because the bulk of this material remained in the fissures and only minor amounts of it penetrated porous wall rocks. The bitumens that occupy the fissures are probably from 1 to 5% of the organic matter in the shales that is soluble, rather than from the insoluble kerogen. Comparisons of the composition of this soluble material extracted from the oil shales show it is similar to the bitumens in the associated veins (Hunt et al., 1954). It has been calculated that only 1/10 of the organic matter in shales adjacent to the gilsonite veins would more than fill these veins. Initially these bitumens were buried under a pressure equivalent to a depth varying from possibly 6000 ft for albrite, to 2000 ft for wurtzilite. As the area was uplifted, tectonic cracks developed tending to create reduced pressure voids into which the bitumens moved. The bitumens moved as viscous fluids and subsequently became solids through inspissation, polymerization, oxidation, or some combination of these processes.

The bitumen deposits undoubtedly were formed simultaneously with the fissures that they fill. It is inconceivable that tremendous fissures, such as those occupied by the gilsonite deposits, could have existed for any length of time without becoming filled with debris from the soft shales, clays, and slightly indurated sands that determine their upper limit. The principal fissures were formed as the basin warped following deposition of the lacustrine sediments and was coincident with uplift in the surrounding Wasatch and Uinta Mountains and Uncompahgre Plateau. The upper parts of the St. Louis and Fort Duchesne gilsonite veins near Fort Duchesne are in the Duchesne River Formation. These fissures could not have been formed earlier than in late Oligocene time. They most likely are of Miocene age, that is, they were formed during the Laramide orogeny. There are no features indicating that there was more than one period of major fracturing of the Tertiary formations of the Uinta Basin, therefore, it is probable that all of the bitumen deposits are of about the same age.

Composition of the Bitumens of the Uinta Basin

Types and classification of bitumens—Bituminous substances are generally divided into two major classes, those soluble, and those insoluble, in carbon disulfide (Abraham, 1945). Subdivisions of these major classes are made on the basis of the fusibility of the substance. In Fig. 3 is presented a classification of most of the known types of naturally occurring bitumens. The crude oils and oil seeps are low molecular weight, volatile bitumens, whereas all the rest of the substances are high molecular weight, non-volatile bitumens. Going across the chart from left to right there is a decrease in the solubility and an increase in the fusion point and the carbon to hydrogen ratio of the bitumens.

Ozocerite is a mineral wax composed principally of straight chain paraffin hydrocarbons with a few naphthenes. Hatchettite and scheerelite are local names for varieties of ozocerite found in Scotland and Switzerland. Montana wax is a mixture of high molecular weight acids and esters 01 the range from about C29 to C35. It is not found in a free state but is Attracted from lignite or pyropissite by solvents. Ozocerite is the only mineral wax found in the Uinta Basin. It is called Utah wax in the literature to distinguish it from Galician ozocerite.

Viscous liquids or solid low-melting bitumens are classified by Abraham as asphaltics. The asphaltics that are readily extracted from asphaltic
sandstones and limestones also come under this classification. Among the asphalt found in the Uinta Basin are: tabbyite, a solid found in veins in Tabby Canyon; a semi-solid bitumen oozing from a creek bed west of Duchesne and called "liverite" in this paper; liquid gilsonite found at depths in the Bonanza gilsonite mine; and argulite, an asphak saturating sandstone in the canyon of Argyle Creek south of Ouray. There are also asphaltic limestones north of Colton and asphaltic sandstones at many other places in the basin. Some of these contain up to 50% asphalt by volume.

An asphalt with a fusing point higher than 230°F is classified as an asphaltite. Gilsonite is the only asphaltite found in the Uinta Basin.

Bituminous substances that decompose before they melt are called pyrobitumens. The asphaltic pyrobitumens are differentiated from the non-asphalts or coals, in that the former generally contain less than 5% oxygen. Wurtzilite, "ingramite", and albertite (also called nigrite) are the principal asphaltic pyrobitumens found in the Uinta Basin.

**FIG. 3. Terminology and classification of naturally occurring hydrocarbons (adapted from H. Abraham, 1945).**

The bitumens listed in Fig. 3 can be separated into fractions on the basis of their solubility in organic solvents. When the bitumen is mixed with petroleum ether it separates into a soluble portion (malthenes) and an insoluble portion (asphaltenes). The malthenes can be further subdivided by mixing them with adsorbent clay and extracting with carbon tetrachloride. The extracts are the oily constituents and the residues are the asphaltic resins. The resins are removed from the clay with carbon disulfide. When the asphaltites are mixed with carbon disulfide they separate into a soluble portion (carbenes) and an insoluble portion (carboids).

**Physical and chemical properties—General properties.** The different bitumens of the Uinta Basin vary considerably in their physical and chemical properties which provide a means for characterizing and identifying them. Table 1 shows the variation in solubility, fusing point, specific gravity, fixed carbon content, and elemental analysis. The bitumens are arranged in order of increasing fusing point: waxes, asphalts, asphaltites, and pyrobitumens. The fusing points increase rapidly for the denser bitumens. Different grades of gilsonite range in fusing point from 230 to 350°F. Solubilities in carbon disulfide show a sharp break between the soluble asphaltite, gilsonite, and the insoluble pyrobitumen, wurtzilite.

The fixed carbon content is defined as the carbon residue left after heating the bitumen at 950°C for 7 min in the absence of air. It is useful in making a preliminary classification of the bitumen. In general it stays within definite limits for the different types of bitumens. Some of the fixed carbon analyses made on Uinta Basin samples are listed in Table 2. These values are on an ash-free basis.

**TABLE 2**

<table>
<thead>
<tr>
<th>Bitumen</th>
<th>Source</th>
<th>Wt. % carbon residue*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozocerite</td>
<td>Soldier Summit</td>
<td>4.1</td>
</tr>
<tr>
<td>Wurtzilite</td>
<td>Country Summit</td>
<td>5.9</td>
</tr>
<tr>
<td>Wurtzilite</td>
<td>Powtin Vein</td>
<td>6.2</td>
</tr>
<tr>
<td>Wurtzilite</td>
<td>Canyon Gentlemen</td>
<td>7.6</td>
</tr>
<tr>
<td>Ingramite</td>
<td>Soldier Summit</td>
<td>8.1</td>
</tr>
<tr>
<td>Ingramite</td>
<td>Soldier Summit</td>
<td>8.4</td>
</tr>
<tr>
<td>Gilsonite</td>
<td>Black Dragon</td>
<td>13.8</td>
</tr>
<tr>
<td>Gilsonite (pencillated)</td>
<td>Bonanza</td>
<td>16.3</td>
</tr>
<tr>
<td>Gilsonite</td>
<td>Bonanza</td>
<td>16.6</td>
</tr>
<tr>
<td>Gilsonite</td>
<td>Weaver</td>
<td>18.6</td>
</tr>
<tr>
<td>Alberite</td>
<td>Soldier Summit</td>
<td>38.0</td>
</tr>
<tr>
<td>Alberite</td>
<td>Soldier Summit</td>
<td>37.7</td>
</tr>
</tbody>
</table>

* Ash-free basis.

Albertites are readily distinguished from the other bitumens by their high carbon residues. Different types of gilsonites differ only by a few percent in their carbon residues. Wurtzilites and Ingramites have unusually low residues considering the fact that both are pyrobitumens.

The refractive index of a bitumen is useful as a correlation index and as an indication of molecular structure. Within any one molecular weight fraction the order of increasing refractive indices is paraffins, naphthenes, and aromatics. In the high molecular weight ranges there is some overlap but the rule still applies generally. Figure 4 is a frequency distribution chart of the refractive indices of ninety bitumen samples. These samples were chosen from as many different localities as possible so as to obtain a completely random distribution. The length of each bar in Fig. 4 indicates...
the number of samples having that particular refractive index. It is apparent, however, that with refractive indices alone it is possible to distinguish between the bitumens of different types.

When the median refractive index of the bitumens is plotted against the fixed carbon content, the points fall in a smooth curve as shown in Fig. 5. Ozocerite, with a high paramin content, has a low refractive index and carbon residue. At points higher on the curve, where the indices and carbon contents are high, there is a decrease in the paramin content and an increase in the aromatic and condensed ring structures. The position of the two pyrobitumens, wurtzilite and ingramite, at the low end of the curve strongly suggests that they either have fewer aromatics in their structure, or smaller molecular units than either gilsonite or albertite. There is other evidence to support this, such as the carbon to hydrogen ratios for wurtzilite and ingramite, as will be shown later, indicate the

![FIG. 4. Frequency distribution of the refractive indices of Uinta Basin bitumens.](image)

![FIG. 5. Refractive index and fixed carbon content of the Uinta Basin bitumens.](image)

Structure correlations from infrared absorption spectra. Additional information on organic structures of bitumens can be obtained from a study of their infrared spectra. Specific atomic configurations, such as an —OH, C=O, and phenyl groups, have absorption bands in specific regions of the spectrum. For example, the —OH group of alcohols absorbs at a wave length of 3.0 μ, the C=O of ketones, aldehydes, Md acids at about 5.9 μ, oxygenated structures in the region of 8-10 μ, ftonatic structures from 11 to 13.5 μ, and long chain aliphatic paraffins Sound 13.9 μ. The ratios of aromatic and paraffinic structures can be determined among bitumens from the intensity of absorption bands in the 11-13.5 μ aromatic region and in the 13.9 ft paramin region. A considerable amount of data on the correlation of atomic groups and infrared absorption frequencies has been reported in the literature (Faraday Society, 1945;
In general, the order of compound having increasing intensities of absorption bands is naphthenes, paraffin^ olefins, aromatics, oxygen, sulfur, and nitrogen compounds. The liquid bitumens have absorption bands approximately twenty times more intense than paraffin hydrocarbons.

The liquid bitumens of the Uinta Basin have essentially the same basic structures as the soluble portion of the solids. Evidence for their similarity is provided by the similarity of their infrared spectra. Structures in the carbon disulfide soluble portions of the Uinta Basin bitumens can be determined by examination of the curves in Fig. 6. The absorption peaks at 13.9 μ in the spectra of ozocerite, wurtzilite, albertite and ingramite indicate the presence of chains of five or more carbon atoms in these compounds. The sharp peaks at about 13.4 μ in the ingramite and albertite spectra are attributed to polycyclic aromatics. The two broad humps at 11.5 and 12.3 μ are due to aromatics, the latter peak being attributed to para-substituted aromatics. The peaks at 8.6 and 8.65 μ in the spectrum of gilsonite, and at 8.9 μ in the spectrum of wurtzilite, are probably due to oxygenated compounds which absorb strongly in the 8-10μ region. The sharp peaks at about 5.9 μ in the spectra of ingramite and albertite are due to the >C=0 group.

Elements analyses. Some information about the molecular structures of bitumens from the Uinta Basin can be obtained from an analysis for the I elements carbon, hydrogen, sulfur, and nitrogen. The ratio of hydrogen to carbon atoms varies in different hydrocarbon structures. Naphthene and paraffin hydrocarbons have high H/C ratios, whereas condensed aromatics have low H/C ratios. Consequently, bituminous substances rich in the former structures have high H/C ratios, whereas carbonaceous substances rich in the latter have low H/C ratios. Ozocerite, a paraffin wax, has the highest H/C atomic ratio of the Uinta Basin bitumens, whereas albertite, the pyrobitumen, has the lowest ratio next to the coals. The ratios of these and other natural bitumens are listed in Table 3.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Source</th>
<th>Atomic H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ozocerite</td>
<td>Soldier Summit</td>
<td>1.96</td>
</tr>
<tr>
<td>2. Ozocerite</td>
<td>Miller Mine</td>
<td>1.89</td>
</tr>
<tr>
<td>3. Tabbyite</td>
<td>Tabby Canyon</td>
<td>1.62</td>
</tr>
<tr>
<td>4. Ingramite</td>
<td>Soldier Summit</td>
<td>1.62</td>
</tr>
<tr>
<td>5. Wurtzilite</td>
<td>Indian Canyon</td>
<td>1.60</td>
</tr>
<tr>
<td>6. Wurtzilite</td>
<td>Red Creek</td>
<td>1.59</td>
</tr>
<tr>
<td>7. Gilsonite</td>
<td>Black Dragon</td>
<td>1.47</td>
</tr>
<tr>
<td>8. Gilsonite</td>
<td>Bonanza</td>
<td>1.45</td>
</tr>
<tr>
<td>9. Gilsonite</td>
<td>Rainbow</td>
<td>1.42</td>
</tr>
<tr>
<td>10. Albertite</td>
<td>Soldier Summit</td>
<td>1.32</td>
</tr>
<tr>
<td>11. Albertite</td>
<td>Albert Co., New Brunswick, Canada</td>
<td>1.24</td>
</tr>
<tr>
<td>12. Coal</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td>13. Bituminous Coal</td>
<td>Uinta Basin</td>
<td>0.80</td>
</tr>
<tr>
<td>14. Anthracite</td>
<td></td>
<td>0.56</td>
</tr>
</tbody>
</table>
The order in which the substances are listed in Table 3 represents an order of decreasing paraffinicity and increasing aromaticity.

Structural interpretations based on H/C ratios are valid only if the total quantity of nitrogen, sulfur, and oxygen in the substances being compared does not differ appreciably. Since these elements replace hydrogen, a pure hydrocarbon structure would have a higher H/C ratio than a corresponding structure containing N, S, or O. Maximum differences in the N, S, O content of the Uinta Basin bitumens are about 6%, which is too low to influence the order in Table 3. The Uinta Basin coal, and bituminous coal, with a high (10-15%) N, S, O content, would have H/C ratios closer to 1.28 and 1.05, respectively, on a N, S, O free basis.

The bitumens with low H/C ratios are generally more insoluble and infusible than those with high H/C ratios. Wurtzilite is a notable exception to this rule having a higher H/C ratio than gilsonite, but being more insoluble. Solubility and fusibility are influenced by other factors, such as the sulfur, nitrogen, and oxygen content of the bitumens.

The sulfur and nitrogen contents of the Uinta Basin bitumens are shown in Fig. 8. Wurtzilite has the highest sulfur content, by far, of the entire group, averaging about ten times as much sulfur as gilsonite. The presence of sulfur linkages in the wurtzilite structure is believed to lead to its rubbery properties and its insolubility and infusibility. Sulfur is known to cross-link large hydrocarbon molecules, as in natural or synthetic rubber, imparting rigidity and insolubility to the material.
the extent of polymerization. Inasmuch as asphaltenes are of high molecular weight, an increase in the average molecular weight of the substances occurs with an increase in asphaltenes. Liquid asphalts are low in asphaltenes and the hard solid asphalts are high in asphaltenes; consequently asphaltenes can be used to measure the change from liquid to semi-solid to solid which represents various stages of weathering.

Separation of hydrocarbons from bitumens by chromatography. The chromatographic procedure involves dissolving the bitumen in some light hydrocarbon, such as n-heptane, and passing it through a column of activated alumina. This is followed by benzene and methanol, ether, or pyridine. The heptane removes the paraffin and naphthene hydrocarbons; the benzene, the aromatic hydrocarbons; and the methanol, the nitrogen, oxygen, and sulfur compounds (non-hydrocarbons). The separations are not quantitative and it usually is necessary to repeat the procedure to obtain an accurate analysis. The approximate distribution of hydrocarbon types in ozocerite and liquid gilsonite by this method is shown in Table 4. The high paraffinicity of ozocerite and the aromaticity of gilsonite are evident from these data. Infrared analyses of the chromatographic fractions also showed that there are paraffin chains in the aromatic, and in the nitrogen, sulfur, and oxygen compounds of ozocerite.

<table>
<thead>
<tr>
<th>Compound type</th>
<th>Weight percentage in Ozocerite</th>
<th>Weight percentage in Liquid gilsonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin and naphthene hydrocarbons</td>
<td>81</td>
<td>18</td>
</tr>
<tr>
<td>Aromatic hydrocarbons</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>Nitrogen, sulfur, and oxygen compounds*</td>
<td>9</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* May contain some hydrocarbons not eluted by heptane or benzene.</td>
</tr>
</tbody>
</table>

Summary of compositional data. The Uinta Basin bitumens are complex mixtures of high molecular weight hydrocarbons and non-hydrocarbons which can be separated into fractions consisting of an oily medium, asphaltic resins, asphaltenes, and carboids. These groups merge into one another and their atomic H/C ratios decrease with each succeeding Member, except for the carboids which differ mainly in having more
oxygen than the asphaltenes. The asphaltenes are usually aromatic, the asphaltic resins are aromatic or naphthenic, and the oily medium may be naphthenic or paraffinic in structure. The molecular weights of these groups vary from about 500 for the oily medium and resins to 30,000 for the asphaltenes, and probably higher for the carboids.

The distinct differences in the Uinta Basin bitumens are due to the differences in the structural units forming the constituent groups. Although asphaltenes are usually aromatic, they may have naphthenes in them. Likewise, the oily medium may be more aromatic than naphthenic or paraffinic, and sulfur or nitrogen linkages may be introduced in the units. Sulfur, particularly, can act as a crosslinking agent to impart rigidity and insolubility to the bitumen. A description of the probable structures of the individual Uinta Basin bitumens based on all available data is presented below.

**Ozocerite** is composed principally of straight and branched chain saturated hydrocarbons with some naphthene groups. The sum of oxygen, nitrogen, and sulfur averages less than 0.5%. The H/C ratio of 1.96 is approximately that of the \(-\text{CH}_2\) — group. The low refractive index, low carbon residue, and absence of aromatic peaks and presence of a strong paraffinic peak in the infrared spectra identify a predominantly paraffinic material. The presence of ceresin wax crystals under the microscope and the infrared band at 7.6 \(\text{n}\) indicate that some branched chain and naphthenic groups are present. The chain length deduced from melting point and X-ray data is in the \(\text{C}_{25}-\text{C}_{35}\) range.

**Gilsonite** is predominantly aromatic, containing condensed ring aromatic structures in the high molecular weight asphaltene fraction and simpler dinaphthyl structures in the oil constituents and resins. It has few paraffins in the oily constituents. Both nitrogen and oxygen linkages are present, and sulfur, particularly, can act as a crosslinking agent to impart rigidity and insolubility to the bitumen.

### TABLE 5.1

<table>
<thead>
<tr>
<th>Serial no.</th>
<th>Bitumens</th>
<th>Deposit and Location</th>
<th>Ash, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>247613</td>
<td>Albertite</td>
<td>NE 1/4 sec. 23, T.10S., R.8E. Salt Lake Meridian</td>
<td>0.3</td>
</tr>
<tr>
<td>222075</td>
<td>Gilsonite</td>
<td>Rainbow Vein, Dragon Mine, Green River Fm., Uinta Fm.</td>
<td>0.3</td>
</tr>
<tr>
<td>211050</td>
<td>Gilsonite</td>
<td>Rainbow Vein, Rainbow Mine, Uinta Fm.</td>
<td>0.1</td>
</tr>
<tr>
<td>69276</td>
<td>Gilsonite</td>
<td>Cowboy Vein</td>
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<tr>
<td>222073</td>
<td>Gilsonite</td>
<td>Wagonhound Vein</td>
<td>0.1</td>
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<tr>
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<td>Gilsonite</td>
<td>Fort Duchesne Vein</td>
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</tr>
<tr>
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<tr>
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<td>Wurtzilite</td>
<td>Lake Canyon</td>
<td>0.05</td>
</tr>
<tr>
<td>96059</td>
<td>Rock</td>
<td>Asphalt Ridge</td>
<td>0.49</td>
</tr>
<tr>
<td>223235</td>
<td>Asphalt</td>
<td>Sunnyside</td>
<td>0.3</td>
</tr>
<tr>
<td>96046</td>
<td>Asphalt</td>
<td>PR Springs</td>
<td>0.37</td>
</tr>
</tbody>
</table>

**Composition of Ash (Bell, 1960)**

<table>
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<tr>
<th>Serial no.</th>
<th>Bitumens</th>
<th>Deposit and Location</th>
<th>Ash, %</th>
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<td>211050</td>
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<tr>
<td>69276</td>
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<td>222073</td>
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<td>Wagonhound Vein</td>
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<td>223230</td>
<td>Gilsonite</td>
<td>Fort Duchesne Vein</td>
<td>0.09</td>
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<tr>
<td>223228</td>
<td>Gilsonite</td>
<td>Pleasant Valley Mine, NW 1/4 sec. 24, T.11S., R.8E. Salt Lake Meridian</td>
<td>0.1</td>
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<tr>
<td>222299</td>
<td>Gilsonite</td>
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<td>0.37</td>
</tr>
</tbody>
</table>

particularly in the higher molecular weight fractions, but the sulfur content is low. Some carbonyl and other oxygenated compounds are present in the oily constituents and resins. Over 50% of the solid gilsonite probably consists of non-hydrocarbons.

The high carbon residue and re-act index indicate that condensed rings are present. The low atomic H/C ratio of 1.42 establishes the aromatic character of gilsonite. Infrared spectra show the presence of carbonyl and oxygenated compounds, and the absence of long paraffin chain structures. The elemental analysis shows that gilsonite is high in oxygen and has the highest nitrogen content of the Uinta Basin bitumens. The solubility of gilsonite in CS₂ establishes that it is not purely a condensed ring system.

Wurtzilite is naphthenic in character with naphthene rings rather than aromatic rings predominating in the higher molecular weight fractions. Chains of five or more \( -\text{CH}_2- \) groups are attached to the naphthene units in both the oily constituents and the asphaltene. Wurtzite contains some oxygen, probably in the form of carbonyl side chains and oxygen bridges. It also has a high sulfur content (4%). The low carbon residue and refractive index and the high atomic H/C ratio of 1.60 definitely establish that wurtzilite has very few condensed ring aromatics.

In its structure, the strong infrared absorption peaks in the aromatic region at 11.5 and 12.3 \( \mu \) u further substantiates this conclusion. Its insolubility and insusibility probably arise from the joining of units of naphthene rings with sulfur and oxygen acting as crosslinking units. The absence of strong infrared absorption peaks due to paraffin units of naphthene rings with sulfur and oxygen acting as crosslinking units. The presence of strong infrared absorption peaks due to paraffin chains, \( \tilde{C}=0 \), and other oxygen linkages establishes that these groups are present in wurtzilite.

Albertite is composed predominantly of condensed aromatic ring structures with the oily constituents containing polycyclic aromatics, carbonayl groups, and some paraffin chains. It has less sulfur and nitrogen than any Other Uinta Basin bitumen except ozocerite.

The very high carbon residue, high refractive index, and low atomic H/C ratio establish the presence of the condensed aromatic rings. The insolubility and insusibility of albertite indicate the condensed rings to be of several more units than in gilsonite. The infrared spectra of the oily constituents and asphaltene establish the presence of carbonyl groups, polycyclic aromatics, and some paraffin chains.

Ingramite appears to be a less polymerized form of albertite. The oily constituents and asphaltene of Ingramite have the same spectra as those of the soluble fraction of albertite, but Ingramite has a higher atomic H/C ratio and lower carbon residue than albertite. These properties would be characteristic of a less polymerized form.

Tabbyite has an infrared spectrum similar to gilsonite except that the weaker infrared peaks in the carbon-oxygen regions indicate fewer oxygenated compounds are present in tabbyite. In all one may find a general discussion on the composition of the anthraxolite. Ontario Bureau of Mines, Rept. 6, 159-161.

References


CHAPTER 9

GEOCHEMISTRY OF ORGANIC PIGMENTS

by H. N. DUNNING

Central Research Laboratories, General Mills Inc., Minneapolis 13, Minnesota

Porphyrs

Introduction—Porphyrins form the basic structural units of respiratory catalysts throughout the plant and animal kingdoms. Chlorophyll, the green pigment of plants, is the agent of photosynthesis and allows the fixation of solar energy in the form of carbohydrates and other food materials. Furthermore, it appears that photosynthesis or related processes indirectly account for the fixation of solar energy in the form of petroleum and bituminous substances—the fossil fuels that supply much of the energy on which our civilization depends. Hemoglobin, the red pigment of blood, is the respiratory pigment of high animals; transporting oxygen and waste products it allows their efficient operation. A third series of pigments, less understood but closely related to hemoglobin, is comprised of enzymes such as the cytochromes that participate in the regulation of cellular respiration. Present-day civilization, therefore, depends on hemoglobin-type pigments for life processes and on chlorophyll-type pigments for energy sources.

The activities of the respiratory pigments are accounted for in part by the metals with which they are complexed. Iron is characteristic of the respiratory pigments of animals, and magnesium is the metal involved in the basic plant process, photosynthesis.

The structures of the "life" pigments are quite similar. Hemoglobin is comprised of heme, a porphyrin complexed with ferrous iron, and globin, a slightly basic, water-soluble protein. Enzymes of the cytochrome system contain the same type of "heme" as hemoglobin, combined with different proteins. Chlorophyll contains a chlorin (a porphyrin in which one double bond of a pyrrole group has been saturated by the addition of two hydrogen atoms) complexed with magnesium and having a phytol alcohol group (C_{20}H_{39}OH) instead of a protein group. The structures of chlorophyll and hemin are shown in Fig. 1.

Proof of structure of these pigments and the chemistry of their porphyrin constituents resulted from the extensive efforts of many workers notable among whom were W. Kuster, R. Willstatter, and Hans Fischer. Hoppe-Seyler (1871) prepared the first porphyrin, originally named the class, and showed the relationship of chlorophyll to hemoglobin by obtaining a