ORGANIC CONSTITUENTS OF OIL SHALES
AND RELATED ROCKS

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INDUSTRIAL HISTORY.

The distillation of oil from shales on an industrial basis has been hindered by the rapid and extensive development of petroleum wells. Now that a limitation of the future supply of oils by wells is foreseen, attention is being directed to the commercial possibilities of bituminous shales as a source of petroleum fuels.

It is recorded that as early as 1694, Eele, Hancock, and Portlock distilled "oyle" from a "stone" which may have been oil shale. Bituminous shales were distilled for the production of oils for medicinal purposes in 1761.

Although the oil shale industry has been best developed in Scotland, the earliest commercial development was in France.[1] In 1830, Lamont obtained paraffin from the distillation of oil shales. The industry began upon the completion of a process for distillation by Sellegue 1839. It continued to grow until 1864 when it was given a set back by the importation of cheao American oils. In 1893 the French government cut in half the import duty on petroleum which caused a still greater check upon the industry. There was a slight stimulation by the high prices during the world war and in 1919 and 1920. At present the import duty on petroleum in France is high.

The development of oil shale distillation in Scotland was not in any way influenced by that of France.[1,2.] James Young had been asked to erect works over a spring of petroleum from a coal pit in Derbyshire. The oil began to fail in about two years. This caused Young to conceive the idea that oil was a product of coal and had been distilled from the latter by subterranean heat. Upon the discovery of a highly bituminous coal called "Boghead coal" or "Torbenehill mineral", he succeeded in producing oil artificially from this coal. In 1850, Young and two associates erected a plant for the production of oil from Boghead coal. The industry developed rapidly and was very successful until 1862 when the "Boghead coal" deposits began to be exhausted. It was then necessary to resort to other materials. Shale began to be used.

As in France, the production of oil from shale was crippled by the importation of cheap petroleum. But in Scotland, the industry was maintained by the consolidations of various companies, by the development of more efficient and economical apparatus and methods, and by the strictest economy in mining, retorting, and refining. At present all the existing Scottish refineries are in full operation.

The industry began in Australia in 1856. The process of retorting soon gave way, to a certain extent, to the exportation of high grade shale for the enrichment of gas. Some companies were discontinued, others merged until finally the corporation, John Fell and Company, controlled most of the work. At first there was much trouble in using the Scottish retorts which were fractured by the intumescence of the shale. New types of retorts were built which overcame the difficulties. In 1923, it was considered that the industry would have to stop because of the high cost of labor and low price of oils.

In Germany, the distillation of tar was known as early as 1778, but not on a commercial scale.[3] Carl von Reichenback gave a great impetus to the work by his discovery of paraffin in 1830. In the fifties, the distillation of tar from bituminous rocks continued to grow in Austria and Germany. Dry-distillation plants had been established in the Rhineland for treating coal. Many of them were later discontinued largely because they made no analytical examination of the raw material. Carl Riebeck in 1858 set up a plant, later enlarged it and continueing to work with untiring energy succeeded in raising the industry to a high position.

Throughout the history of the Saxon-Thuringian mineral-oil industry, there has been a continued retrogression in the price of its products. The present market is very depressed.

The industry was developed in the United States previous to the discovery of the Pennsylvania oil fields.[4] There were between fifty and sixty plants operating which used the Scotch process. These plants were located in Massachusetts, New York, Pennsylvania, Ohio, Kentucky, Virginia, Connecticut, and West Virginia. At the same time, several plants were operating in Canada.

SCIENTIFIC THEORIES AND INVESTIGATIONS.

Much experimental work is now being done in the efforts to find more profitable processes of distillation. At the same time investigations are being made to determine the origin of oil shales as shown by a careful examination of their contents. While the latter investigations may seem at first glance to be of purely scientific value, their results will no doubt throw much light upon the problems of commercial distillation.

T.W.E.David of the Geological Survey of New South Wales began his investigation of the kerosene shales of New South Wales in 1865 and was one of the first to advance a theory of the algal origin of bituminous shales.[5] The kerosene shales are a variety of torbanite. David's microscopic investigation showed spherical bodies which he considered to be sporangia and particles of resin which he thought might be spores, seeds or pollen grains. He concluded that this material must have originated in showers of pollen grains, sporangia, spores, and seeds which became admixed with peaty material from swampy ground. David later discovered aggregations of club-shaped bodies resembling the zoospores of algae. From these discoveries he proposed the theory that kerosene shale was probably formed in lakes from either sporangia or algae.

Bertrand and Renault, French botanists, in their study of thin sections of boghead mineral from Torbanehill, Autun, and New South Wales discovered orange or yellow bodies embedded in a matrix of brown ulmic material.[5] These orange and yellow bodies were determined to be the remains of a free alga thallus known as Reinschia. Between the thalli were some macerated spores and pollen grains. Bertrand considered that such materials must have been accumulated in absolutely still surroundings, in very shallow water, and in a very short space of time since otherwise fermentation and decay must have set in. The gelosic algae formed gelatinous precipitates on the surfaces of lakes and swamps. Spores, pollen grains, plant cells, cuticles, and vegetable debris also helped to compose this gelatinous mass.

There was at first much objection to an algal theory of origin of boghead because of the nature of algal material which is very easily attacked by the agents of decomposition. At a later date, Reinhardt Thiessen supported the theory with discoveries made in a detailed examination of boghead coal.

Thiessen, now of the United States Bureau of Mines, has confirmed the theory by making comparisons with a colonial blue-green algae now existing in the salt lakes and salt lagoons of southern Australia.[6] At the end of the winter, the green scum formed by the algae is blown to the southern shores of the lakes. When the lakes evaporate, the algal material dries up into a rubber-like mass called coorongite. Careful examination of the cellular structure has shown that where several colonies are joined there is no protoplasm within the cells. The cell walls which consist largely of oily substances, instead of decaying upon exposure to the air, form a rubbery, elastic mass. Upon distillation, coorongite yields 97 percent of volatile matter from which may be condensed a quantity of oil. The microscopic examination of boghead coals showed a significant resemblance to the coorongite material.

Charles A. Davis has described the structureless organic material to be found in thin sections of Green River shales as the remains of microscopic algae, mixed with pollen which have passed into a jelly-like phase due to the activities of bacteria and other organism.[7] From this, he reached the conclusion that the material was laid down originally in water and passed through stages of decomposition before stratification and lithification.

Jeffrey placed the origin of most coals in lakes or lagoons in which the floating material sank to the bottom.[8] The muck included spores and pollen grains from firs, pine, and spruce. Later aquatic plants such as water lilies and finally debris from land plants added to the accumulation. He considered tasmanite a pure spore coal in which he had discovered microscopically uncollapsed spores, partially collapsed spores, and spores entirely collapsed. One section showed the walls thick, another section showed the walls thick and rough. Jeffrey did not accredit the theory that the latter might be algae since they occurred side by side with modified remains of wood. He examined cannel coal sections which showed spore bodies and dark crinkled bands which were the remains of wood and which might be called lignitoid. In ordinary bituminous and anthracite coal, the lignitoid was most abundant. Jeffrey believed that his investigations gave evidence of three constituents in coal: spores, lignitoid, and unmodified carbonized wood. The coals rich in spores are petroliferous.

Dawson, formerly Professor of Natural Science at McGill College, has made statements concerning the importance of spores and spore-cases in the origin of bitumens[9]. His conclusions were based on observations of the coals of Nova Scotia and Cape Breton, of bituminous shales from Kettle Point, Lake Huron, and of coals and shales from Ohio. The oldest beds of spore-cases known to Dawson were in the shale from Kettle Point, Lake Huron. The spore-cases appeared like flattened discs, amber in color, slightly papillate externally, and with a point of attachment on one side. The only structure shown was that of the spore walls surrounding internal cavities which enclosed flocculent or granular matter. He found great quantities of spore-cases the size of mustard seeds. Out of eighty-one coals, such bodies were recognized in sixteen. Similar amber-colored discs were recognized in a layer of cannel coal near Glasgow. The specimens from Ohio indicated that spores are not essential to coal.accumulation but form a greater proportion in shales and cannel coals. Dawson maintained that in general, coal contains the outer bark of trees and cuticle of many other plants both of which are highly carbonaceous, and that the spores and spore cases are important constituents of shales and cannel coals.

H.R.J.Conacher thinks that the yellow bodies found in many shales and torbanites are resins which were originally formed by secretions in plant canals, cells, stems, leaves, fruits, and from wounds, the resin fragments from cells being more or less spherical and those from canals in needle-like rods.[10] Conacher claims that the appearance of structure in these resins may be due to internal shrinkage from evaporation, to pressure, and to minute bubbles of gas.

E. Cunningham Craig, in "Oil Finding", offers a theory as to the origin of shales which differs essentially from all other theories. It is based on the principle of adsorption. Fine clays, being colloids, have adsorptive properties. Craig asserts that such clays were impregnated with petroleum which was a sol. This petroleum became concentrated by the loss of some of the lighter hydrocarbons and was adsorbed by the clays forming a gel-like mass. To quote from "Oil Finding";"Given a colloid deposit and the colloid solution, sufficiently concentrated, in juxtaposition, the result will be an oil shale".

Prof. R.D.George of the University of Colorado performed experiments in the distillation of oil shales in which he discovered that volatile gases were given off in three distinct cycles.[4] The first volatilization occurred in the true hydrocarbons at a comparatively low temperature; the second in the vegetable matter at a higher temperature. It was impossible to determine whether this last was from the true hydrocarbons or the vegetable tissue.

An interesting investigation is being conducted at present by David White and Taisia Stadnichenko. The object of this investigation is to ascertain the relations between the present plant remains in a shale and their original character, to determine the relations between the organic materials and the products of distillation, and to observe the temperatures at which various constituents break down yielding considerable volatile constituents. Microfurnaces have been designed and constructed for this work through the Carnegie Geophysical Laboratory.

PRESERVABLE ORGANIC MATERIAL

Thiessen has defined carbonaceous shale as a shale which contains organic matter;bituminous shale as a shale which contains bituminous matter; an oil shale as one which yields oil and gas upon destructive distillation.[13] It might be added that a second criterion for oil shale is the fact that oils cannot be extracted by solvents. The most recent investigations concerning the relation of the organic matter to the products of distillation lead to the probable conclusion that the process of distillation produces oil from the accumulated residue of various kinds of organic matter in shale.

MICROSCOPIC INVESTIGATIONS OF SHALES.

General Classification.

It is the purpose of this paper to describe the organic contents as seen in thin sections from a representative collection of bituminous and carbonaceous rocks including oil shales, torbanites, and cannel coals. The results of the investigation show considerable variety of material found in different shales.

According to the organic constituents, the shales can be placed in the following groups: first, those with an ulmic groundmass with wax disseminated throughout, with remains of cuticles, and with carbonized fragments; second, shales similar to those of the first type except that they also contain conspicuous lumps of resins and waxes; fhird, shales containing an ulmic groundmass, carbonized fragments, and some yellow spores; fourth, shales which are chiefly composed of yellow spore bodies in an ulmic groundmass; fifth, shales containing chiefly large yellow wax lumps which do not show any indication of structure; sixth, those shales which also contain large portions of wax, but with indications of structure in the wax; and seventh, a very unusual type in which the wax seems to be in the form of crystals

Wax and resins are both found in the organic residues of the oil shales. "Waxes occur as exudations on the leaves, stems, and fibres of plants". Resins occur in all parts of the plant but chiefly in the bark. Resins, oils, fats and waxes may form an admixture. It is very difficult if not impossible to determine one from the other under the microscope.

Chemically, wax is a monobasic acid of high molecular weight linked to an alcohol of high molecular weight. No such definite statement can be made describing a resin.

In respect to physical differences, waxes liquify more rapidly than resins. Crystallinity has been observed in some waxes, but resins are always amorphous. Resins are solid translucent and break with a conchoidal fracture. Rosin possesses a vitreous luster and is very brittle.

DESCRIPTIONS

The first named group includes several of the different shales from the Green River formation, shales from the Dunnet oil shale seam and the Fells oil shale seam of Scotland, from the Kimmeridge shale of Dorset, England, and from the gray bituminous shale of Rosevale, New Brunswick.

There were some forty slides examined from the Green River formation for which there were no megascopic specimens. These had been taken from Parachute Creek, Conn Creek, and Kimball Creek. A Leitz Wetzlar polarizing microscope with a magnification of 150 diameters was used for the greater part of all microscopic observations except in a few specific instances.

The groundmass shown by nearly all these slides varies from yellow to rich brown. The yellow color is probably due to fine particles of wax disseminated throughout the entire mass. The rich brown is undoubtedly a mass of ulmic material, which varies in amount in different slides. In some cases, it is spread rather evenly over the entire surface; in other instances, it is concentrated in patches. Frequently, there is a directional structure, the material being arranged parallel with the stratification of the shale.

A few slides show short, thin, wavy streaks of dark brown. It was concluded that these are humic precipitates.

The color suggests greater bituminization or devolatilization tending to a greater proportion of fixed carbon.

Many sections show an abundance of rich brown leaf-like material in large, irregular patches. These are partially humified and carbonized remains of plant cuticles. There are also large round and thick-walled bodies of dark brown, evidently the heavy coverings of sporangia. There are several round, dark brown masses with a granular appearance. It is possible that these may be aggregates of pollen grains.

There are many carbonized fragments having joints as though portions of jointed stems. One slide shows a perfectly preserved portion of carbonized cell structure. There are several dark oval bodies showing points of attachment.

A few sections show no organic structures at all. They present an agate-like appearance due to wavy banding of ulmic material and reddish wax or resin.

Shales were examined from the mahogany band near the mouth of Parachute Creek. They are dark, brownish gray, light brown where weathered, dull in luster, with a texture which is waxy in streaks, with moderate toughness, with an uneven and conchoidal fracture, with distinct stratification, and with a specific gravity of 1.59 at the top of the band, 1.11 near the middle, and 1.63 near the exposed surface. In the Bunsen flame, the mahogany shales burn easily, giving a bituminous odor.

Microscopically, these shales are similar to the other Green River shales already described. They show the same ulmic groundmass filled with fine particles of yellow wax, streaks of dark brown humic precipitate, remains of spore-cases, carbonized plant fragments, and occasionally the agate-like banding.

The brownish shale from the Naval Reserve, Garfield County, Colorado is a dense, brownish gray rock with a dull luster, moderate toughness, distinct stratification, waxy scratch, uneven fracture, and a specific gravity of 1.60. It ignites easily in the Bunsen flame and continues burning for a short time after being removed from the flame.

In thin section, the brownish shale shows a greater proportion of mineral content than the other shales of Colorado. The groundmass is yellow; through this are scattered streaks of dark brown ulmic material.

The large specimen of shale from the black mahogany streak, Kimball Creek, Garfield County is dense, black, waxy in luster, moderately tough, easily inflammable, with little visible evidence of stratification, with a waxy scratch, with conchoidal fracture, and with a specific gravity of 1.45.

Microscopic examination shows a dark rich brown ulmic groundmass banded in wavy streaks. Fragments of carbonized outlines of cell structures can be seen very clearly. There are many small, black carbonized grains, probably pollen. There are several carbonized fragments giving evidence of plant structure but not specifically indentifiable.

The shale from the mahogany shales, Naval Reserve Colorado shows the characteristics of this group. Megascopically, this shale is dense, brownish gray, with a dull to waxy luster, moderate toughness, distinct stratification which gives the shale the appearance of wood or agate. It breaks with an uneven and conchoidal fracture, and has a specific gravity ranging through 1.53, 1.60, and 1.62. The shale is easily inflammable.

Thin sections show the groundmass varying from yellow to brown with wax scattered throughout and often with ulmic material. Some slides are very lean in organic material, others very rich. There are frequently streaks of humic precipitate. There are reddish-brown patches of cuticle remains. Evidences of the remains of spore-cases and the exines of pollen occur often, in one instance near a great cluster of black dots which may be carbonized remnants of pollen grains. One section shows reddish-brown streaks of wax.

The Florissant shale from Colorado was not examined megascopically. The thin section shows a groundmass with l light brown ulmic material scattered throughout. There are carbonaceous patches and some brown fragments of cuticles.

Bradley describes the organic contents of the shore phases of Green River shales as the remains of planktonic organisms that lived in the surface waters of ancient lakes.[14] These organisms were probably microscopic plants. He also states that pollen and spores are much less abundant than the remains of plankton. Davis describes the material of the Green River shales as having originated in collections of plant debris, largely from microscopic algae, which passed into a jelly-like phase.[7] The particular sections described in this paper do not give any indication of a colonial structure which might be characteristic of algae. In looking for material to verify the results described in this paper, it was found that in the description of the research now being conducted by David White and Taisia Stadnichenko, mention is made of an oil shale from Parachute Creek; in this the contents are given as ulmic groundmass, brown cuticles, pale amber-colored spores, some resins, occasional chitinous scales of insect larvae, and rarely algal groups.[12]

The megascopic description of the shale from the Dunnet oil shale seam, Linlithgowshire, Scotland is as follows: color, dark grayish brown to nearly black; texture, dense; luster, dull, earthy, waxy; toughness, moderate; stratification, distinct in some cases, not distinct in others; scratch, waxy; fracture, conchoidal and uneven; specific gravity1.92 to 2.08; inflammability, ignites after a short time in the Bunsen flame.

The microscope shows the shale from the Dunnet oil shale seam to be similar to the Green River shales. The brown ulmic groundmass contains yellow wax in fine particles. There is a considerable variety of carbonized plant fragments. Large patches of black dots are probably carbonized pollen grains. One fragment shows the thick walls of a stem enclosing cellular structure. Another looks like a plant carpel. Others appear like much twisted ribbons.

Fells oil shale seam,Tarbrax, Midlothian, Scotland produces a tough, dense, very dark gray shale with a luster varying through dull and waxy, with a conchoidal and uneven, fracture, an indistinct stratification, a waxy scratch and a specific gravity of 1.93. It ignites easily in the Bunsen flame.

Under the microscope, the Fells shale shows a brown ulmic background full of irregular brown and black patches and small, black, rod-like remains. The brown and black patches are undoubtedly masses of humified and carbonized vegetable dibris; the black rods fragments of plant structures such as root fibers.

The gray bituminous shale from Rosevale, New Brunswick is dense. very dark slaty gray, dull to waxy, moderately tough, not clearly stratified, inflammable, with conchoidal fracture, with a waxy scratch, and with a specific gravity of 2.09.

The thin section shows yellowish brown material in considerable quantity and mixed with grains of mineral matter. There are a few patches of yellow and orange, these probably wax and resin. Black fragments suggest organic structures.

Only the microscopic examination was made of the Kimmeridge shale from Dorset, England. The whole groundmass is a rich orange or reddish-brown showing that it contains ulmic matter mixed with much waxy and resinous material. One of the slides shows many lenticular resinous and waxy bodies. This makes it doubtful whether the shale should be placed in this general type of oil shales or in the second group to be described later. There are streaks of dark brown humic precipitate and an abundance of carbonaceous material without definite organic structure.

The second group of shales, those with an ulmic groundmass, cuticular material, carbonaceous remnants, and lumps of wax and resin, includes a few Green River shales, the Kimmeridge shale from Clavell's Head, England, the Broxburn shales, and Pumpherston shales.

Of the Green River shales, two slides for which there are no hand specimens belong to this group. The entire groundmass of these thin sections appears perfectly black; evidently it has a large proportion of highly carbonized material mixed with the ulmic. In this are many yellow, russet brown and orange lumps of wax and resin, which are usually long, narrow, and lenticular showing a tendency to parallel arrangement.

The oil shale from Rosevale is dense, grayish black, having a dull to waxy luster, moderate toughness, barely discernible stratification, waxy scratch, sub-conchoidal fracture and a specific gravity of 1.79.It ignites easily in the Bunsen flame.

The thin section shows a yellow to light brown groundmass with much mineral matter. Patches of yellow and orange wax occur in places. There are many carbonized fragments of plant strucuture such as portions of stems, cross sections of fibers, fragments which look like cross sections of seeds and of pinnules, a body of wax which seems to be in the part of the plant in which it was originally secreted. No specific identification of such fragments can be made with any degree of certainty.

Kimmeridge shale from Clavell's Head, England gives a specific gravity of 1.29. The color is very dark gray; the texture fine-grained; the luster dull and earthy, occasionally waxy; the toughness moderate; the stratification fairly distinct; the scratch waxy; and the fracture uneven. The shale burns easily.

The groundmass of the thin section contains chiefly orange wax arranged in much elongated lenticular masses. This is a shale which comes between the first group of shales and the second, for some slides show a groundmass similar to that described for the Kimmeridge shale from Dorset, except, perhaps, that it has a greater proportion of wax. In all the slides structureless, highly carbonized, and humic materials are mixed in with the wax. There are many clusters of black dots, black rod-like fragments, ribbon-like coils, portions of root-fibers and of stems. Such fragments have been carbonized.

The Broxburn shale is very dark gray; varies in luster through dull and waxy; is tough and easily inflammable. The fracture is conchoidal and uneven; the scratch waxy; and the stratification discernible. The specific gravity varies from 1.36 to 1.72.

The thin sections show the groundmass to contain considerable ulmic material mixed with wax. Lumps of wax occur in places. Many carbonized fragments may be observed some of which enclose lumps of wax. A long, reddish-brown mass of cuticle with very clearly discernible tissue occurs in one section.

The Kamp's shale from Scotland is dense, nearly black, moderately tough and has a dull luster. It breaks with an uneven to sub-conchoidal fracture, ignites easily, and is distinctly stratified. The specific gravity is 2.02.

The thin sections which are across the stratification show an abundance of brown ulmic material arranged with a tendency toward directional structure. There are streaks of humic precipitate. The shales contain irregular patches of yellow wax. One perfectly round russet patch shows slight evidence of structure. Several carbonized plant fragments may be seen.

The Pumpherston shale, also from Scotland, is dense, very dark gray, dull, and tough; has a distinct stratification, subconchoidal fracture, waxy scratch, and specific gravity of 2.21. The rock is easily inflammable in the Bunsen flame.

The microscope shows a very patchy mass of brown ulmic products through which are scattered small lumps of yellow wax. One section shows a long and broad band of yellow wax with a granular aspect probably caused by mineral grains. Long irregular masses of russet color are probably remains of cuticles. Carbonized fragments of plant structures occur frequently.

The Devonian shale from Montgomery County, Kentucky, and the black bituminous shales from the Albert Mines, New Brunswick make up the third group of shales, those with an ulmic groundmass, carbonized fragments, and some yellow spore exines.

The hand specimens of the Devonian shale are black, dense, tough, easily inflammable, and dull in luster. The fracture is conchoidal and uneven; the scratch waxy; and the stratification discernible but not distinct. The specific gravity is 2.03.

Under the microscope, the Devonian shale shows much brown ulmic matter and several yellow spore exines. When the section is cut across the stratification, the spore exines show that they have collapsed. Russet-brown cuticle remains and carbonized plant fragments are common.

The black bituminous shale from the Albert Mines, New Brunswick is dense, tough; has a dull to waxy luster, distinct stratification, conchoidal fracture, and specific gravity varying from 1.57 to 1.76. The shale is easily inflammable.

The organic constituents consist of much brown ulmic matter, collapsed yellow and orange spores, small orange-colored portions of macerated spores, and carbonized fragments of stems, petioles, and fibers.

The Devonian black shales and cannel coal from Kentucky are excellent examples of shales predominating in yellow spore exines contained in an ulmic groundmass. These shales and coals have been the objects of much investigation.

The Devonian black shale is a dense black rock with a dull luster. It is tough and does not show a distinct stratification. The scratch is waxy, and the fracture conchoidal.

All the thin sections show a dense, brown ulmic groundmass. The sections cut parallel to the stratification contain round, bright yellow bodies, sometimes brown in the center, sometimes yellow clear through, the former evidently showing the hollow cross sections of the spore exines. Some of the exines are entire; others are only fragments. The sections cut across the stratification show that the spore coverings are collapsed, their lengths corresponding to the diameters of yellow bodies in the parallel sections. Frequently, the yellow material suggests cellular structure. Some russet-colored bodies can be observed. These are round with an ulmic center. The russet-colored part suggests a radiating structure. They may possibly be cross sections of woody stems or very thick walled spores. There are some carbonized fragments of stem and a little cuticle. The striking feature of these sections is the great abundance of spores.

The Kentucky cannel is black, dense, not at all tough, and very inflammable. It breaks with a conchoidal and an uneven fracture. The luster is waxy and dull; and the scratch is waxy. The stratification is only discernible. One specimen gave a specific gravity of 1.22, another of 1.14. The coal is very easily inflammable.

The thin sections are very similar to those of the Devonian black shales. There is brown ulmic groundmass. The yellow spore bodies are very thick, being round in the sections parallel to the bedding and collapsed in those cut across the bedding. Frequently the upper and lower parts of these yellow bodies have been broken apart. There are numerous orange-brown patches, most of which are elongated parallel to the stratification. These are probably waxy and resinous secretions as are also the irregular yellow patches which appear occasionally.

Thiessen describes cannel coal as containing predominantly spore matter with some cellulosic degradation and resinous matter.[15]

The fifth group of shales may be differentiated by the conspicuous and numerous bodies of yellow wax, which do not give any indication of structure. To this class belong the oil shale from Esthonia and kerosene shale from New Zealand.

The Esthonian shale is light brown and is dense but encloses many small particles of shale. The stratification can hardly be determined. The luster is earthy, but the scratch is waxy. It breaks easily with an uneven fracture. This shale resembles those already described in its easy inflammability. The specific gravity is 1.28.

The thin section shows that it is thick with yellow patches of wax between which are dull brown, granular patches of humic material with inorganic matter. No plant structures can be observed.

The kerosene shale from New Zealand is almost black, fine-grained, fairly tough, and burns easily. The stratification is indistinct, the scratch is waxy, and the fracture conchoidal. The specific gravity was found to be 1.13.

The microscopic section shows the material to be chiefly yellow wax admixed with mineral grains. Brown ulmic material is scattered through this wax in such a manner as to form a reticulated pattern.

The sixth type of shales to be discussed includes those with brown ulmic material and an abundance of yellow wax which suggests structure. To this class belong the kerosene shale from Camden, New South Wales; the stellarite from Nova Scotia; boghead coal from Torbanehill, Scotland; and the torvanite from Wolgan, New South Wales.

The kerosene shale from Camden County, New South Wales is a tough, very fine-grained, almost black shale with an earthy luster. It has a waxy scratch and subconchoidal fracture. The stratification is not distinct. This shale ignites easily in the Bunsen flame, continuing to burn a short time after removal from the flame. The specific gravity is 1.08.

The microscopic examination shows a very dense, dark brown ulmic groundmass, in which is an abundance of large and small irregularly shaped bodies of yellow wax. Structure in the wax is indicated by groups of oval spots, darker in color than the surrounding wax. No inorganic material can be discerned.

The stellarite from Nova Scotia is a brittle, dense black hydrocarbon with a dull to waxy luster and with no visible stratification. It breaks with an uneven fracture. The scratch is waxy, and the material burns easily. The specific gravity was determined to be 1.55.

The groundmass of the thin section is brown. There are numerous round, russet-colored bodies, which have suggestions of lines radiating from the center outward. There is no indication of mineral matter.

The stellarite shales are defined by Abraham as a species of albertite representing a transition between true albertite and cannel coal.[15] Albertite is one of the asphaltic pyrobitumens which are "derived from the metamorphosis of petroleum". The thin section doubtless shows relics of inspissated petroleum in which are bodies of resin.

The boghead coal of Torbanehill, Scotland, is brownish, black, dense, dull, brittle, and easily inflammable. The stratification is discernible, and the shale breaks with a conchoidal fracture. The specific gravity was determined as 1.40.

A larger part of the thin section is almost solid with lighter yellow and deeper yellow patches which are adjacent to each other. There are a few bodies of russet-color. Thin streaks of carbonized material occur in places. The thinner edges of the slide show an indication of colonial structure. This boghead coal is not as typical of the group as any other sections examined because it does not show colonial grouping as clearly. The wax is admixed with mineral matter. The consistency of the two shades of yellow throughout the section may be significant.

The torbanite from Wolgan, New South Wales is black, dense, dull, moderately tough; has no distinct stratification and breaks with a conchoidal fracture. It is the most inflammable of any specimens examined. The specific gravity of the sample is 1.15.

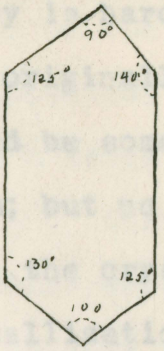
The characteristics of the thin section are very typical of this group. There are many very large and very bright yellow masses of wax which give conspicuous indications of colonial structures. There are numerous groups of darker colored oval spots which seem to have a concentric arrangement. The very dark brown groundmass separates the yellow masses which are lobed, thus indicating still further the algal grouping.

Craig considers torbanite to be composed of vegetable debris and says it is a special form of cannel coal.[11] According to his theory, it consists of a coal matrix in which are hydrocarbons combined with inorganic matter. They have been formed from uncarbonized vegetable debris mixed with argillaceous sediment, sealed, and subjected to pressure. Globules of incipient petroleum formed, making gels with the inorganic colloid material. Thus Craig considers torbanite to be an arrested first stage of petroleum.

The most widely accepted theory of the formation of torbanite is that of an algal origin as advanced by Bertrand and Renault, David, Thiessen, and others. The colonial markings seen in the masses of yellow wax are suggestions of groups of algae.

Examination was made of a very unusual rock occurring in a thin stratum above the mahogany shale of the Naval Reserve, Colorado. For convenience the rock will be termed analcite sedimentary rock. It is light brown in color, dense, dull, tough, and not as easily inflammable as the others examined because of a smaller organic content but capable of burning in small sections and giving a strong bituminous odor. It has no stratification, has a brittle scratch, breaks with an uneven fracture, and weathers to almost white. The specific gravity was determined as 2.26.

The microscopic section shows an abundance of colorless, isotropic, six-sided crystals which resemble analcite. Chemical analysis supports the conclusion that these crystals are analcite. The interstitial groundmass is chiefly analcite also. Scattered through the groundmass sometimes projecting into the analcite crystals and occasionally surrounded by them, are many crystals of dark brown material of organic origin. They are smaller than the analcite crystals and of a different crystallographic form. They suggest either prism faces combined with pyramid faces or pinacoidal faces with domes. The accompanying sketch was made from one of the most typical crystals.



A portion of a thin section was burned and found to contain a carbon residue where the organic material had been.

Upon distillation, hydrocarbon gases, ammonia water, and heavy oil were given off. The odor was very disagreeable suggesting pyridine in the content.

It was impossible to dissolve any of the organic material although carbon tetrachloride, carbon disulphide, petroleum ether, alcohol, diethyl ether, naphtha, and turpentine were tried. In this respect, the organic material of the crystals corresponds to the regular organic material of the Green River shales.

The origin of this rock is most difficult to determine. The migration of petroleum through a shale might leave inspissated relics in cavities formerly occupied by a mineral.

In that case, the cavities would not all be entirely filled by the organic material. These sections, however, do not show any crystals that are not entirely filled. Hence, this theory is hardly tenable. On the other hand, if the crystals were originally of the dark material now observed, there should be some slight indication of pleochroism and anisotropism; but no such phenomena occur. It is difficult to explain the crystallization of hydrocarbon accompanying the crystallization of analcite. It is equally hard to account for the presence of analcite in a sedimentary rock. Analcite is a zeolite and has been described in igneous rocks. From the available data, the question of origin can onlybe presented without an attempt at a final solution.

COMPARISON OF ORGANIC MATERIAL.

In this investigation of the several shales, the relative importance of different kinds of organic constituents was noted. Humic material is to be observed in all the specimens examined. In all cases, it is a dominant factor in the groundmass although varying in amount enough to produce a gradation in color from light yellowish-brown to the darkest brown. The latter type shows no mixture with mineral grains; the former frequently does.

The carbonized material does not at any time constitute more than an extremely small part of the organic constituents. Often it is entirely absent. It was noted in about 40 percent of the total number of slides. Of this percentage, nearly one-half was from the Green River shales.

Organic structures of some kind occur in varying proportions in many of the shales observed. The carbonized fragments occur only in small quantities. Cuticle remains may be negligible in amount or may comprise as much as one-fourth of the total area seen under the microscope. In the few instances in which algal structure may be observed, it forms a large part of the total mass.

Carbonized fragments which undoubtedly showed structure were observed in about 29 percent of all the slides, forming very small proportions of the organic matter in each slide as previously mentioned. Cuticular remains were seen in 25 percent of the sections. This percentage, however, was formed almost entirely by the Green River shales. Algal structure was observed in sections from only four kinds of shales.

Spores occur in the Devonian shale, the Devonian black shale, the bituminous black shale, and the Kentucky cannel. Out of these four deposits, the spores are very abundant in only two. They may occur abundantly in a macerated form mixed with the humic material and not definitely recognized.

With the exception of a very few sections which were specifically mentioned, the amount of organic matter exceeds that of the mineral matter.

A portion of mahogany shale from the Naval Reserve, Colorado was found to weigh 1.2 gm. This same piece was freed from inorganic matter by recognized methods. After this it was found to weigh .6 gm. The difference in weight after the removal of the inorganic constituents shows that organic matter comprises one-half of the shale by weight. Since the average specific gravity of the mineral composition is 2.6 and that of the organic content could not exceed that of bituminous coal, which averages about 1.4, the organic matter would greatly exceed the mineral matter in volume. The shales vary from this proportion to that of the New South Wales shales which show no mineral matter under the microscope.

DISTILLATION EXPERIMENTS.

A few simple experiments were made with the mahogany shale from the Naval Reserve, Colorado with a view to ascertaining whether wax is the only organic constituent important in the production of petroleum or whether the other organic constituents are also important in the distillation of shale oil.

The raw shale was broken into very small pieces and placed in a test tube. The shale was distilled over a Bunsen flame and gave off inflammable hydrocarbon gases and a measurable amount of a heavy, black petroleum with a very disagreeable odor, indicating a pyridine content.

Sections of the shale as thin as one-thirty second inch were boiled with hhdrochloric acid and then treated with hydrofluoric acid for a period of five weeks. They were then boiled with nitric acid. A spongy mass resulted which hardened into a porous form. A few pieces of this were placed in a closed tube and distilled over the Bunsen flame, yielding an appreciable amount of heavy, dark petroleum and inflammable gas and giving the same disagreeable odor as that produced in the first distillation. The proportion between the amount of material distilled and the yield of oil was about the same as that of the first distillation.

Another section of the mahogany shale was boiled in concentrated nitric acid until it was converted into a swollen, pulpy, porous mass, which, when magnified, showed the pockets from which the mineral had been dissolved. Water was poured into the beaker still containing the nitric acid in which the shale had been boiled. After a few moments, the liquid was decanted and a coating of brown wax was found lining the sides of the beaker. This was preserved for distillation, which will be described later. The material which had been digested with the nitric acid was next subjected to the treatment by the organic solvents, naphtha, carbon tetrachloride, and petroleum ether. The carbon tetrachloride and the petroleum ether extracted some wax so that much, if not all, of the wax was now removed from the original shale.

This organic residue was next distilled over the Bunsen flame. A yielding of several drops of shale oil was obtained from a thin piece of the residue about one-half inch long and one-eighth inch wide, also inflammable hydrocarbon gas. The odor was not as disagreeable as in the other distillation.

From this it is evident that wax is not the only organic constituent which yields petroleum upon distillation.

The wax recovered from the shale treated with nitric acid,as previously described, was distilled. A few small pieces in the end of a closed tube yielded a few drops of petroleum, giving an odor similar to that observed in the distillation of the raw shale.

These experiments show that distillation products may be obtained from unorganized organic residues. The investigation of the analcite sedimentary rock shows that a definite, organized chemical compound can exist and can be distilled.

CONCLUSIONS.

The results of this investigation support a general theory of the organic origin of oil shales, differing specifically in the type of vegetable debris accumulated and in the modifications which such debris has undergone. It is evident that organic remnants were gathered together under conditions favorable for their preservation. Swamps, marshes, and lagoons would be most advantageous for such conditions. That the vegetable accumulation was subjected to a certain amount of bacterial action is proved by the predominance of humic material in all the thin sections. Into these swampy lands was brought a certain amount of sediment which was mixed with the organic residues. Certain types of vegetation such as algae might form a very dense residue held together by gelatinous material. This would not easily mix with the mineral constituents except to form a colloidal mass with the kaolin content. The accumulation might also result from the wind-blown spores from the land vegetation or a more varied planktonic mass of debris. With these types the sediments might mix more easily.

The specific types of organic constituents form a good basis for the classification of pyrobituminous rocks. This is especially true since the present investigations indicate that the organic constituents control the distillates produced by the various oil shales.

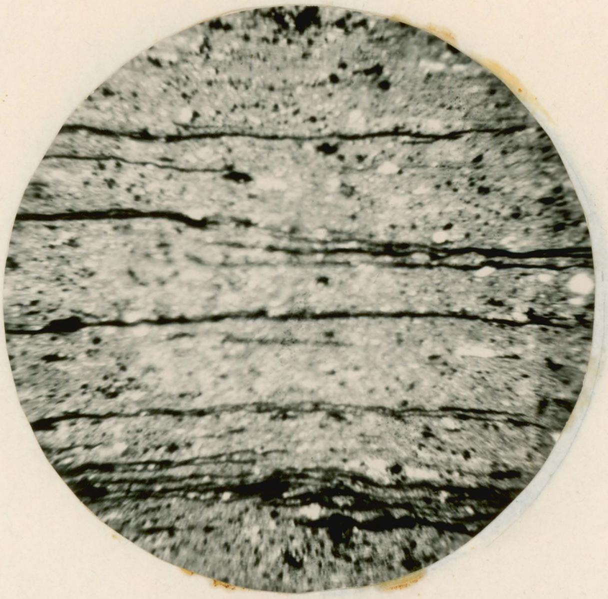


Figure 1.-Photomicrograph of Green River shale(x150), showing streaks of humic precipitate.

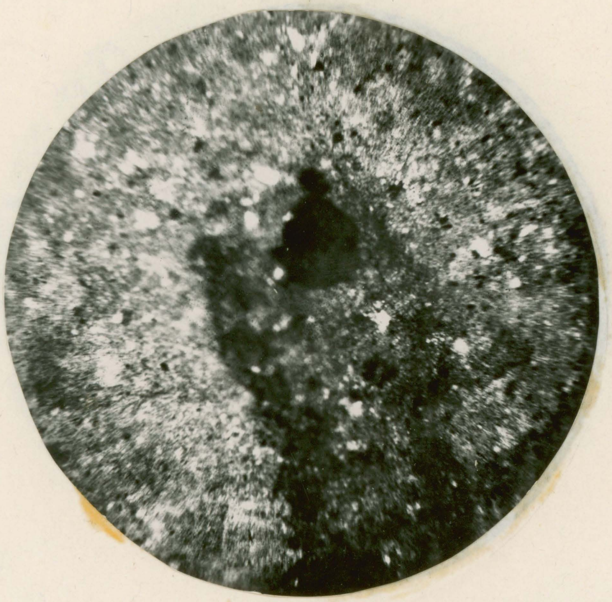


Figure 2.-Photomicrograph of Green River shale(x150), showing covering of sporangium.

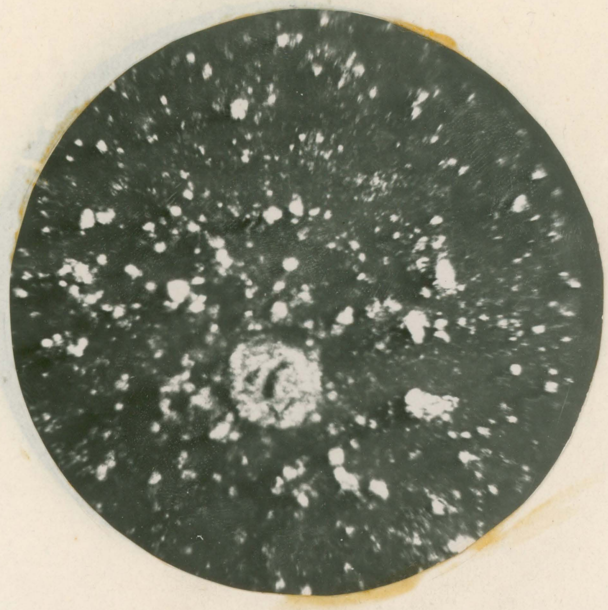


Figure 3.-Photomicrograph of Devonian black shale(x150), showing large yellow spore.

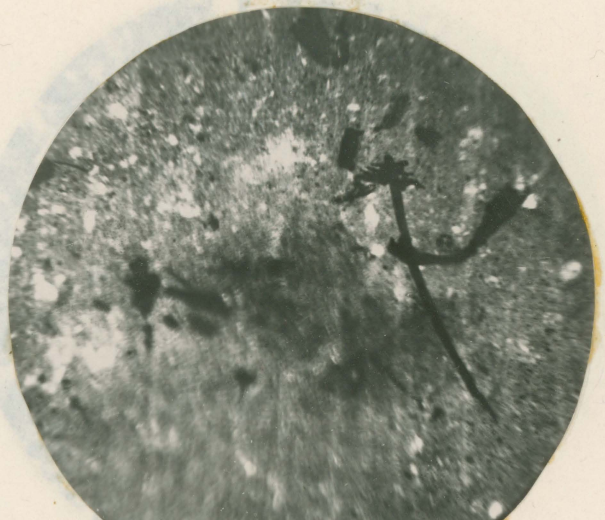


Figure 4.-Photomicrograph of Dunnet shale(x150), showing carbonized fragments.

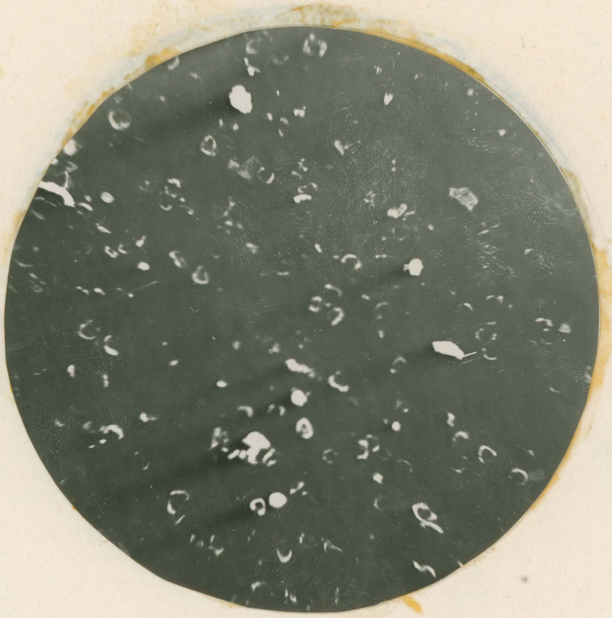


Figure 5.-Photomicrograph of Kentucky cannel(x150)

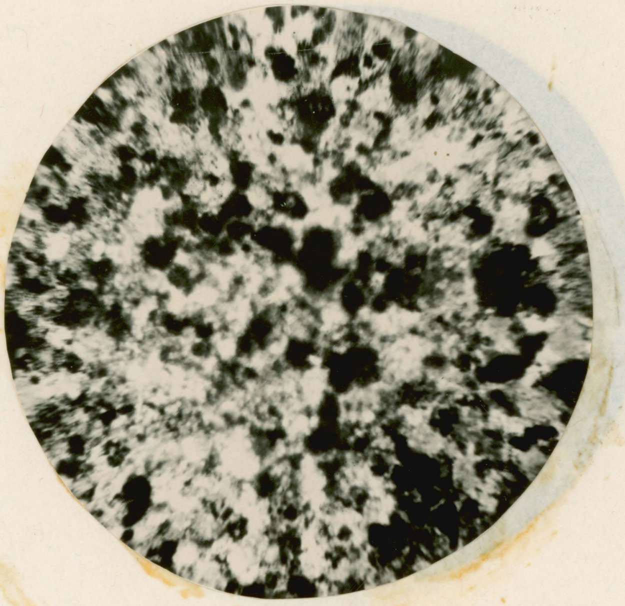


Figure 6.-Photomicrograph of Esthonian shale(x150)

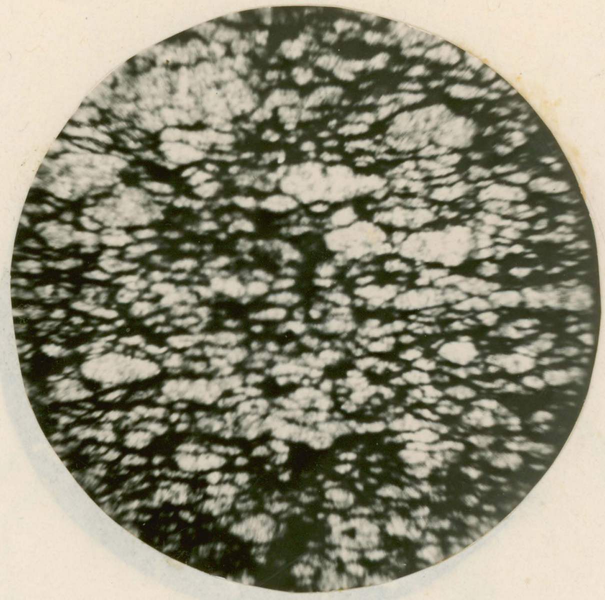


Figure 7.-Photomicrograph of New Zealand shale(x150)

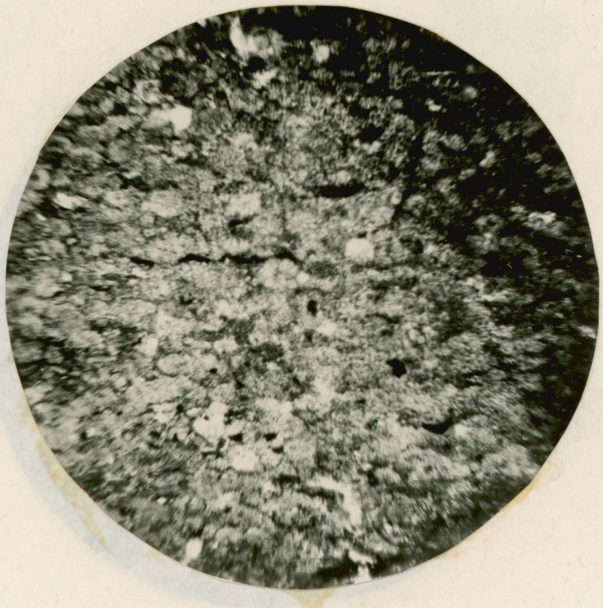


Figure 8.-Photomicrograph of boghead coal from Torbanehill, Scotland(x150)

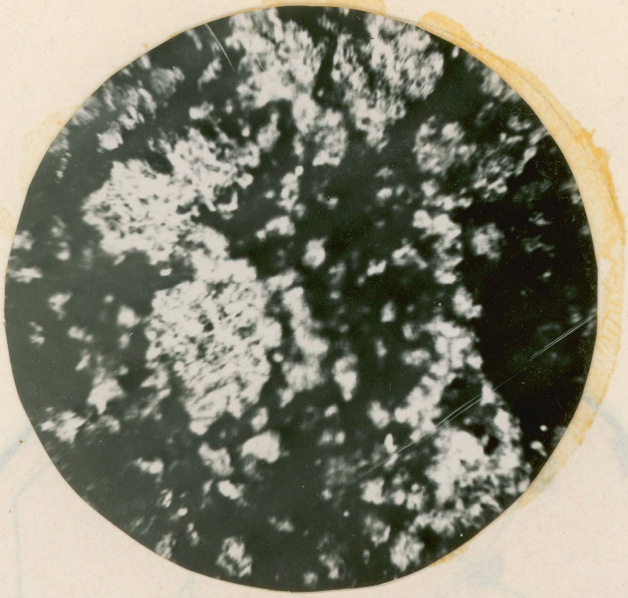


Figure 9.-Photomicrograph of torbanite from New South Wales(x150)

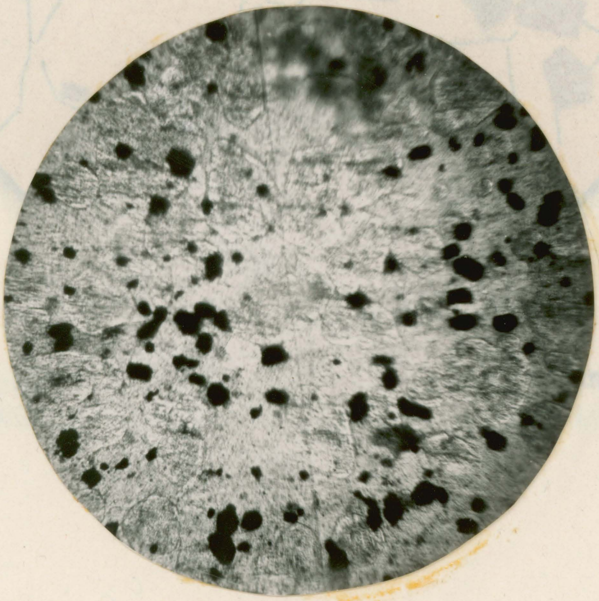


Figure 10.-Photomicrograph of analcite sedimentary rock(x150)

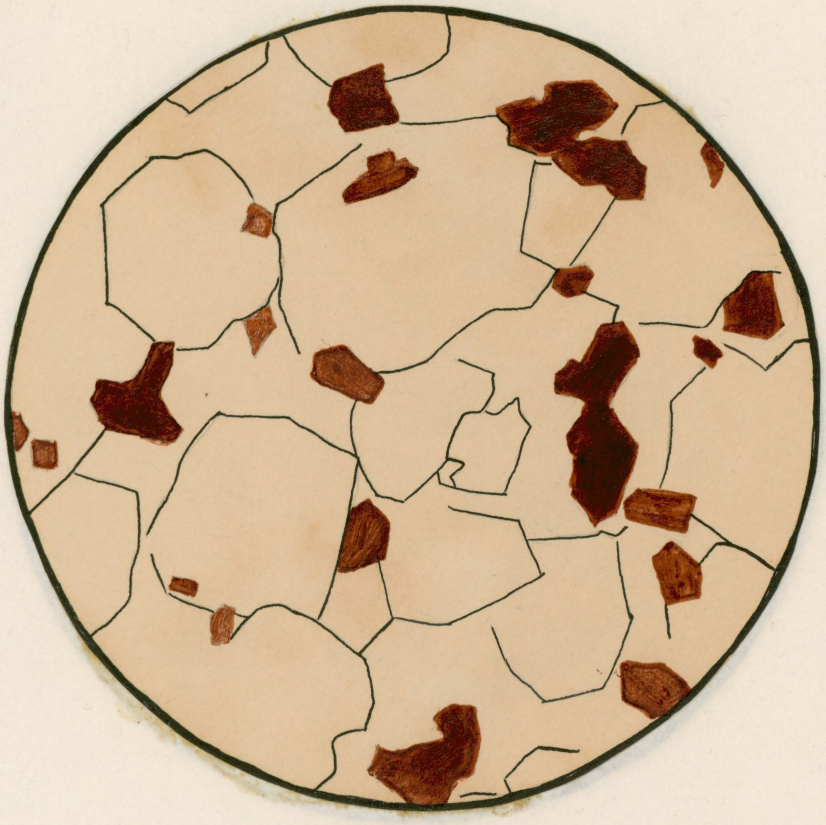


Figure 11.-Camera lucida drawing of analcite sedimentary rock(x240)

Figure 12.-Drawing of Green River shale (x230), showing preserved cell structure

Figure 13.-Drawing of New Zealand shale
(x230)

Figure 14.-Drawing of stellarite from Nova Scotia(x230)

Figure 15.-Drawing of torbanite from New South Wales(x230)

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