UNITED STATES

DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

# OIL YIELD AND CHEMICAL COMPOSITION OF SHALE FROM NORTHERN ALASKA

by

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66-131

Open file

1965

This report is preliminary and has not been reviewed for conformity with U. S. Geological Survey standards and nomenclature.

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## Illustration

Figure 1. Locations of oil shale samples in northern Alaska

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Table 1. Location and description of samples of oil shale from central Brooks Range, northern Alaska

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3. Chemical composition of 12 samples of oil shale from central Brooks Range, northern Alaska, and samples of the Green River, Chattanooga, and Pierre and Bearpaw Shales for comparison

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5. Fischer assays and semiquantitative spectrographic analyses of samples of oil shale from western Brooks Range, northern Alaska

# Oil yield and chemical composition of shale from northern Alaska

By Harry A. Tourtelot and Irvin L. Tailleur

U.S. Geological Survey[1]

[1] The U.S. Geological Survey is continuing the study of northern Alaska oil shales in cooperation with the Office of Naval Petroleum and Oil Shale Reserves, U.S. Navy, Washington, D. C.

The Arctic Research Laboratory, Barrow, Alaska under contract to the Office of Naval Research provided substantial logistic support in both the 1964 and 1965 seasons.

In a paper published in 1964, Tailleur reported oil yields of 146 and 144 gallons per ton from two samples of marine organic-rich shale from northern Alaska. Such oil yields are exceptionally large; oil yields of about 25 to 50 gallons per ton were obtained from 5 other samples, and 1 sample yielded 7 gallons per ton. Semiquantitative spectrographic analyses of these samples indicated that vanadium, zinc, and molybdenum, as well as some other metals, were present in unusually large amounts compared to other oil shales. The data were so unusual that Tourtelot, in collaboration with Tailleur, obtained additional spectrographic analyses from the small remaining hand specimens of the original samples and made other studies. It became apparent that the shale samples were of considerable geochemical interest.

In the summer of 1964[1], Tailleur was able to collect 12 samples,

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[1] Field studies including collection of samples were continued in the season of 1965. Organic-rich rocks were examined and sampled along nearly the entire north front of the Brooks Range from the Kivalina River on the west to the Nanushuk River in the central foothills region.

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each from 1 to 10 pounds, from some of the localities in the central Brooks Range on which he had first reported, and from other localities from which samples had not been analyzed previously. An integrated investigation of their oil yield, chemical composition with respect to both major constituents and minor elements, mineralogy, and petrology was then undertaken. The large oil yields of 75 to 150 gallons per ton came from an unusual type of organic-rich shale called tasmanite, which consists almost entirely of the fossil remains of a sporelike alga, <u>Tasmanites</u>. The preliminary results of this investigation are presented in tables 1, 2, and 3, and the locations of samples on figure 1.

In addition, oil yields and semiquantitative spectrographic analyses of five samples from Tailleur's current map area in the far-western Brooks Range are reported in tables 4 and 5 and figure 1. Also shown on figure 1 are the locations of hand specimens of organic-rich shale from the western and central Brooks Range contained in available collections at the Menlo Park Center of the Geological Survey. Although analyzed only microscopically, these samples showed that tasmanite is present at two more localities and as clasts in younger detrital rocks and that many of the shale specimens are comparable petrographically in kind and amount of organic material to shale that assayed 25 to 50 gallons per ton.

J. M. Schopf identified the rich oil shale as tasmanite, and provided valuable descriptions of some samples and much helpful information on the nature of the organic material in the samples. R. M. Kosanke has aided Tourtelot in the study of the thin sections and given useful comments on the organic components of the samples.

## Geology

Organic-rich shales are widespread in a belt of intensely and complexly deformed rocks bordering the north edge of the western and central Brooks Range. Outcrops of the shale are poor and reveal contorted, highly disturbed strata with obscured stratigraphic relationships. In general, the beds of interest occur in the stratigraphic interval between the Triassic and the mid-Cretaceous; their special depositional conditions suggest that they are synchronous deposits yet evidence is contradictory. Associated rocks make up different assemblages of chert, shale, and/or wacke that probably represent several stratigraphic sequences juxtaposed by large-scale overthrusts.

Although much of the geology of the oil shales remains to be understood, some order within the samples that have been examined is discernible: The oil shale at localities 1 and 3 underlies with slight unconformity wacke and mudstone equivalent to the Fortress Mountain Formation (Albian-Cretaceous) and appears to be at or near the top of a section of clay shale that contains Early and Late Jurassic (R. W. Imlay and D. L. Jones, written communications, 1963 and 1964) fossils. The organic shale at locality 2 is associated with clay shale and with coquinoid limestone beds of Buchia assigned to the Valanginian (Cretaceous) (D. L. Jones, written communication, 1964) and underlies the same Fortress Mountain-equivalents that are present at localities 1 and 3. The oil shale at localities 5, 6, 7, and 8 is interbedded in a chert section that apparently succeeds the Triassic Shublik Formation and underlies somewhat arenitic rocks with Valanginian Buchia as well as equivalents of the Fortress Mountain Formation; the organic beds at locality 4 could represent either the same section or the lower part of the Shublik Formation. The tasmanite, Tasmanites itself being nondiagnostic as to age, at localities 12, 14, 16, 22, and 23 is included in a section of varicolored chert that lies between carbonate and lutitic rocks which are of Late Paleozoic age and the Okpikruak Formation which contains Buchia assigned to the Berriasian (Early Cretaceous). The oil shale or organic-rich shale at localities 11, 13, 21, and 24 is associated with chert which apparently underlies a section of clastic rocks that is characterized by wacke with spherical (cannonball) concretions and that could be equivalent to the Okpikruak Formation; nearby blocks of the generally clastic Nuka Formation of Late Paleozoic age suggests a stratigraphic relationship with that formation. The oil shale at localities 10, 15, 18, 19, 20, 26, and 27 is included in a thin section of fine-grained deposits containing fossils of probable Jurassic, possibly Early (R. W. Imlay, written communication, 1964) age, that succeeds the Shublik Formation without recognizable interruption and is succeeded by clay shale with the same coquinoid limestone as at locality 2 and then by the Fortress Mountain Formation.

## Chemical composition

Analyses for samples from the central Brooks Range (tables 2 and 3) differ from those for samples from the western Brooks Range (table 5), and data from the two areas will be discussed separately.

### Central Brooks Range

#### Sample processing

The 12 samples collected by Tailleur in 1964 (tables 1, 2, and 3) were received from the field in blocks and pieces from 3 to 8 inches in maximum dimension and thickness depending on the fissility of the shale. The samples were collected in the field to represent a specific rock type at a specific place. Representative splits were taken in the laboratory from each field sample to represent the lithology of the sample as a whole and set aside for reference and for thin sectioning. Specimens of concretions or those showing other different characteristics of the sample also were set aside.

The remainder of the sample was then rough-crushed and mixed. A half-pint was split out mechanically and ground on a ceramic buckboard to standard analytical fineness. This material was divided into two parts, one for chemical and spectrographic analyses, and one for X-ray analyses. A full pint was split out for Fischer assay and reduced to minus 8 mesh by hammer mill. In this way, the sub-samples for analysis in the several laboratories were made as uniform as possible with respect to the sample received from the field.

## Oil yields and related data

The oil yields of the samples from the central Brooks Range range from about 3 to 144 gallons per ton, or 1 to 55 percent of the rock. The three richest samples came from localities 14 (144 and 89 gals/ton) and 16 (75 gals/ton). The richest sample consists almost entirely of the disseminules of the sporelike fossil, *Tasmanites*. Small amounts of quartz and barite are the only evident nonorganic material. The lesser yields of 89 and 75 gallons per ton also were obtained from tasmanite, but in these samples, the organic material is diluted with quartz that was deposited within the hollow disseminules of the *Tasmanites* before much compaction had taken place. The oil from the tasmanite has a specific gravity of about 0.91 at 15.6°C and the oil flows freely at temperatures a little about 0°C. About 88 percent of the oil remains after heating approximately 1 hour at 55°C. As determined by chromatographic separation on silica gel, almost half of this residue consists of aromatic hydrocarbons, a quarter of saturated hydrocarbons, and the remainder of nonhydrocarbons. From 50 to 85 percent of the organic carbon in the raw shale is evolved as oil or gas in the Fischer assay, which are larger proportions than in any of the other samples that were studied.

The samples from localities 11 and 13 that yield about 45 gallons per ton contain fibrous-appearing red to reddish-brown organic matter. The sample from locality 25, however, that also yields about 45 gallons per ton contains black organic matter that is opaque in thin section. The oils from these samples are similar in composition and character as far as the present data indicate, but the oil from the sample from locality 25 is exceptionally light, having a specific gravity of 0.86 at 15.6°C. Less than 40 percent of the organic carbon in the raw shale of these samples is evolved as oil and gas. Possibly different retorting methods would increase the yield from these samples.

The thin sections of the two samples from locality 11, samples 64ATr207A and 207B, look very similar, both samples appearing to consist almost entirely of fibrous red organic matter. The apparently greater degree of weathering of sample 207B may be the reason why this sample yields only 26 gallons per ton as compared to sample 207A which yields 45 gallons per ton.

## Major constituents

The major constituents in the chemical compositions of the samples from the central Brooks Range (table 3) reflect the mineralogical composition of the samples as indicated by X-ray analyses and petrographic study. All the samples contain small amounts of clay, generally less than 25 percent, except for samples 64APa201D-1 and 64APa201D-2. The alumina contents of these two samples are 11.6 and 14.0 percent respectively, compared to a range of 1.2 to 7 percent for the other samples. Sulfur, reported as total sulfur as $SO_3$, occurs mostly in pyrite in samples 64ATr207A and 207B, in pyrite and barite in samples 64ATr305B and 305C, as well as in small amounts of gypsum in several of the samples. Some of the sulfur in each of the Alaska samples, however, occurs in the organic matter in the shale. The behavior of this sulfur in the distillation process has not been investigated. Some iron probably also is found in the organic matter.

Shale sample 64APa201D-1 contains an anomalously large amount of barium, equivalent to 11 percent barite. Other samples, however, such as 64ATr209B, 64ATr305B, 64ATr305C, contain 3 percent or more barite so that the occurrence of barite must be regarded as common for this group of rocks. Sample 63ATr230 from locality 7 in the western Brooks Range (tables 4 and 5) also contains much barite.

## Minor elements

As a group, the samples of oil shale from the central Brooks Range are unusual with respect to their minor element content compared to other oil shale. In general, the shale approaches marine organic-rich shale in its content of zinc, molybdenum, and vanadium, although the amounts of the individual elements is variable; samples otherwise similar have greatly different zinc contents, for instance. The minor element analyses (table 3) indicate the content of the whole sample and not merely the ash of the organic-rich rock. In considering the amounts of minor elements that might be recovered in connection with distillation processes, and assuming that little or none of most elements would be distilled as organic compounds, the amounts in the whole sample can be calculated to the amounts in the spent shale remaining after Fischer distillation assays (table 2) or to the amounts in the ash if the spent shale were ignited. Sample 64ATr209A, for instance, contains 110 ppm molybdenum, yields 144 gallons of oil per ton, and 26.8 percent of the sample remains as spent shale after distillation. The spent shale thus would contain about 440 ppm molybdenum, an enrichment of about 4 times. The minor element content of the other samples should be similarly enriched in the spent shale by factors of 1.1 to 1.7, according to the percentage of spent shale (table 2). The minor element content of the ash of the whole rock can be estimated by using factors of 1.3 to 7, obtained by dividing 100 by the percent ash in raw shale shown in table 2. The molybdenum content of the ash of sample 64ATr209A would thus be about 630 ppm. The content of minor elements in the ash of some samples is significantly high and should add considerably to the economic value of the shale if the elements can be recovered as a by-product of distillation.

Sample 64ATr305C is richest in copper (380 ppm), selenium (200 ppm), zinc (7000 ppm), silver (4000 parts per billion), and equivalent uranium (70 ppm). The amounts of all these elements, except the uranium measured as equivalent uranium, are more than twice as large as the generally accepted average for black shale. Arsenic (110 ppm), nickel (400 ppm), and vanadium (1700 ppm) also are present in very large amounts, although other samples of Alaska oil shale contain somewhat larger amounts. The minor element content of the closely associated sample 64ATr305B is not unusual except, perhaps, for zinc (420 ppm).

Zinc, copper, and silver are present in large amounts in many marine black shale beds in which fish remains are abundant, the Kupferschiefer being a well-known example. Judging from the phosphorus content of the Alaskan oil shale samples (table 3), fish remains are almost 4 times as abundant in sample 64ATr305C as in sample 305B which is much less than the differences in minor element content between the samples.

The closely related samples 64APa201D-1 and 201D-2 contain large amounts of vanadium (3100 and 1200 ppm), boron (250 and 270 ppm), and chromium, (280 and 430 ppm). The vanadium content of 64APa201D-1 is the highest found and is unusual in that the sample contains the smallest amount of carbon and yields the smallest amount of oil (12.3 percent and 2.9 gallons per ton, table 2) of any of the samples. The relatively large amounts of boron in these samples perhaps is contained in the relatively large amounts of clay.

Of the associated samples 64ATr207A and 207B, sample 207B is anomalous in its contents of arsenic (200 ppm), copper (320 ppm) cobalt (150 ppm), lead (80 ppm) molybdenum (220 ppm), and nickel (450 ppm). Most of these elements commonly occur in sulfide minerals and the sample is rich in pyrite (table 1). Sample 64ATr207A, however, also is rich in pyrite, and its minor element content is not remarkable. No differences between the samples can be made out that would explain the difference in minor element content. The samples are similar in that each contains 150 ppb (parts per billion) gold, the highest amounts found in any of the samples.

The amounts of arsenic (63, 67, and 110 ppm) and molybdenum (110, 170, and 450 ppm) in the three tasmanite samples, 64ATr209A, 209B, and 210 are unusual chiefly in comparison to other marine organic-rich shale inasmuch as the values, except for the 450 ppm molybdenum, are exceeded in other samples of Alaska oil shale. Pyrite is present only in trace amounts in sample 209A so these elements are not related to pyrite. The three samples are uniform in the nature of their organic material. Sample

210 contains the largest amounts of arsenic and molybdenum as well as the largest amount of ash of the three samples (54.1 percent, table 2) but the available mineralogical data do not suggest any mineral known to contain these elements.

Mercury is surprisingly abundant in all samples. Although data on the average mercury content of shale and other nonmineralized rocks are few, unpublished data furnished by J. Howard McCarthy (oral communication) of the U.S. Geological Survey indicate that the expectable mercury background content is less than 100 ppb. The lowest amount of mercury found in the Alaska oil shale samples, 650 ppb in sample 64APa208, if found in soil samples, would suggest a mercury anomaly in mineralized areas, according to Mr. McCarthy. In addition, he adds that soil samples from the center of mercury anomalies near some known deposits do not contain as much as the 3000 ppb mercury reported for samples 64ATr207A and 64ATr209B.

The geochemistry of mercury in black shale is virtually unknown. Organo-mercury compounds seem plausible sources of mercury in such rocks although no relation between the amounts of mercury and amounts of carbon or oil yield is evident in the data on the Alaska oil shale samples. It may be that the climate of northern Alaska minimizes losses of mercury by vaporization on the outcrop, which is a possible cause of loss of mercury from outcrops in warmer climates. It is thus possible that the mercury content of the Alaska oil shale samples represents startling syngenetic concentrations.

The gold content of most sedimentary rocks as well as the earth's crust is generally considered to be on the order of x ppb (0.00x ppm). The values for gold reported in table 3 thus are distinctly anomalous. Sample 64ATr207A has one of the highest gold contents, 150 ppb; and one of the highest mercury contents, 3000 ppb. There is no evident relation between gold and mercury except that all samples contain anomalous amounts of both elements. Nor is there any evident relation between gold and other elements or other characteristics of the samples. According to Garland B. Gott (oral communication), gold values approaching 100 ppb from soil samples seem to outline gold anomalies associated with known gold mineralization in the few areas where gold has been used as a guide element in geochemical prospecting.

The geochemistry of gold in sedimentary rocks, like that of mercury, is virtually unknown. It may be that 100 ppb or so of gold represents the average gold content of metal-rich black shale, such as the Alaska oil shale. Many additional analyses are needed.

The possibility that both the gold and the mercury contents represent epigenetic mineralization cannot be ignored, however. The large difference in zinc and arsenic contents between the associated samples 64ATr305B and 305C, and the differences in arsenic and molybdenum contents among the tasmanite samples, and other similar variations, suggest that the minor element distribution in these samples is perhaps partly the result of processes other than those expected for marine black shale. The alternative hypothesis of epigenetic mineralization may explain the erratic distribution of elements in the samples, but it is not clear why some samples should be more highly mineralized than others.

## Western Brooks Range

The five samples analysed so far from the western Brooks Range have low oil yields, only two yielding more than 20 gallons per ton and the maximum being 24 gallons per ton. In thin sections, the organic matter is reddish brown and fibrous or black and opaque similar to that in thin sections of shale from the central Brooks Range that yield twice as much oil.

Pyrite is in all samples from the western Brooks Range and in larger amounts than in the samples from the central Brooks Range. Dilution of the organic matter by detrital minerals as well as by the pyrite also is more evident and may partly explain the lower oil yields of the western samples.

Sample 63ATr230 from locality 7 contains about 5 percent barite, thus indicating that barite in considerable amounts can be common in organic-rich shale in the western Brooks Range as well as in the central part of the range.

The minor element content of the five samples are indicated only by semiquantitative spectrographic analyses, so the data are subject to revision. A split of each of the original samples and the ash of each sample were analysed separately and both analyses are reported in table 5. The amounts of most minor elements are larger in the ash analyses than in the original analyses within the limits of precision of the semiquantitative spectrographic method. The differences between amounts of elements in the analyses of the ash and in the analyses of the original rock are a function of the ash content of the samples.

The minor element contents of these five samples, as a group, are not so strikingly different from the expectable composition of shale as those in the samples from the central Brooks Range.

Antimony and tin were reported in sample 61ATr28A, the tin being detectable only in the ash of the sample. Antimony, in particular, is an unusual constituent of shale and subsequent analyses indicate that, if actually present, it is very erratically distributed in the rocks.

Silver is reported in the analyses of all samples in larger amounts than could be found in the central Brooks Range samples by more sensitive analytical methods. Molybdenum in amounts of 0.001 to 0.015 percent in the original sample is expectable for organic-rich shale. The 0.2 percent vanadium in the analysis of the original sample 61ATr28A is the largest amount of vanadium found in these samples and represents a considerable concentration compared to other organic-rich shale. The 0.05 to 0.07 percent zinc in samples 63ATr260A and 260B at locality 4 is unusual, and the presence of zinc in only these two samples suggests that zinc may not be a syngenetic constituent.

Other localities

A sample from locality 9 on the Kivalina River in the western Brooks Range (fig. 1) has been reported upon by Stadnichenko (1929) and White (1929) although no oil analyses were given. The sample is described as a brown oil shale containing "a great many spore exines, many of which are twisted" (Stadnichenko, 1929, p. 824). White (1929, p. 844-845) described the spore as Sporangites alaskensis. Winslow (1962, p. 81) later studied the same material and assigned the species to the genus Tasmanites.

Stadnichenko and White both discuss float samples from the mouth of the Meade River near Point Barrow and from the Etivluk River that are identical in every way with the tasmanite samples from localities 12 and 14. Stadnichenko (1929, p. 824) compares the material to tasmanite but does not apply the name. White (1929, p. 845) named the "spore" Sporangites arctica and does not refer to either the genus Tasmanites or to the rock type, tasmanite.

In addition, Stadnichenko and White describe a sample of boghead or algal coal collected as float near the head of the Meade River. Most boghead coals yield large amounts of oil on distillation. No material of this kind has been found so far in the present investigations of the organic-rich shale in the Brooks Range.

An unusually rich oil shale from the Christian River area on the south side of the Brooks Range (loc. 28, fig. 1) was reported by Mertie in 1930 (1930a, p. 138-139). The sample presumably was collected from float and it yielded 122 gallons of oil per ton on standard distillation analysis. This is the highest oil assay reported from North America until Tailleur's 1964 report. The remarkably large oil yield implies that the sample was a tasmanite or a boghead coal. The area has been revisited (W. Brosgé, oral communication) and no similar organic-rich rocks have been found.

Mertie (1930b, p. 131-132) also reports organic-rich shale of Triassic age from Trout Creek (not shown on fig. 1) near the confluence of the Nation River with the Yukon River almost 200 miles southwest of locality 28, that yielded 28 gallons of oil per ton. Stadnichenko (1929, p. 824, 836-838) and White (1929, p. 848) make some additional comments on this sample, White inferring that its oil content was derived from scattered algal colonies.

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