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OIL YIELD AND CHEMICAL COMPOSITION OF SHALE FROM NORTHERN ALASKA

by

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Illustration

Tables

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

[*] 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.

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, *Tasmanites*. 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 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 Cretacecus). 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.

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

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

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

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

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.

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.