Petroleum Hydrocarbons: Generation from Fatty Acid

Abstract. *In the presence or absence of water, behenic acid generates hydrocarbons during heating at 200°C with bentonite. Without water the ratio of isobutane or isopentane to normal butane or normal pentane is much higher than with water. Besides C_{21} and lower* n-*alkanes,* n-*alkanes with 22 to 34 carbon atoms are also formed.*

In connection with the generation of petroleum, several investigators have published data on the formation of hydrocarbons from various types of organic matter in sediments (*1*). Other authors (*2*) have performed model experiments with pure organic compounds. The present investigation also deals with a pure organic compound, a saturated fatty acid.

In many young sediments that have never suffered great depth of burial, the amount of normal (*n*-)alkanes with an odd number of carbon atoms greatly exceeds the amount of those with an even number in the range of about 27 to 37 carbon atoms (*3*). This "odd predominance" depends, among other things, on the depth of burial; with increasing depth the odd predominance decreases and generally disappears. The fact that depth plays such an important role suggests that temperature has a great influence on the formation of *n*-alkanes. It is often thought that these *n*-alkanes are formed from straight-chain fatty acids.

We have studied the formation of hydrocarbons from behenic acid (normal $C_{21}H_{43}COOH$). One gram of this acid was kept at 200°C in a sealed glass tube, with 3 g of bentonite clay as a catalyst, for 89 and 760 hours. The tube was opened in an atmosphere of hydrogen, and the volatile reaction products were stripped off with a stream of hydrogen at 150°C and collected in a vessel placed in liquid nitrogen. This low-molecular-weight fraction was analyzed by gas chromatography. The residue containing the nonvolatile reaction products was subjected to extraction with *n*-pentane. The extract containing the hydrocarbons with a higher molecular weight was passed over a silica-alumina column to obtain the saturated hydrocarbons, which were then separated as the urea adducts into a fraction rich in *n*-alkanes and a fraction containing the branched-chain and cycloalkanes. The *n*-alkane fraction was analyzed by means of gas chromatography.

The amounts of the various components generated after heating are listed in the table.

The total amount of hydrocarbons with 3, 4, or 5 carbon atoms increases in proportion to the duration of the heating. With increasing heating time the amount of saturated hydrocarbons increases very strongly, but the amount of unsaturated hydrocarbons decreases. This suggests that the unsaturates are intermediates in the formation of the saturated hydrocarbons.

Gas chromatography was used to detect the *n*-alkanes from C_{14} up to C_{34} in the fraction with a higher molecular weight. There was a strong predominance of the C_{21} *n*-alkane, which can be attributed to the decarboxylation of the fatty acid. Figure 1 is a distribution diagram of this fraction. The total amount of *n*-alkanes with a higher molecular weight was about 2 mg.

A remarkable thing, however, is that *n*-alkanes with a longer chain than that of the original acid are also present. This suggests that the *n*-alkanes present in crude oil need not necessarily be derived from fatty acids with longer chain lengths.

Table 1. Amounts of low-molecular-weight hydrocarbons generated during heating at 200°C of 1 g of behenic acid with bentonite clay.

Hydrocarbons	Heating period (hr): 89 (μmole)	Heating period (hr): 760 (μmole)
Groups		
C_3	0.18	1.12
C_4	0.29	2.20
C_5	0.33	2.69
Individual compounds		
Propane	0.03	0.87
Propene	0.15	0.25
n-Butane	0.02	0.54
Iso-butane	0.08	1.50
Butenes	0.19	0.16
n-Pentane	0.02	0.38
Iso-pentane	0.07	2.20
Pentenes	0.24	0.11
n-Hexane	0.02	0.29

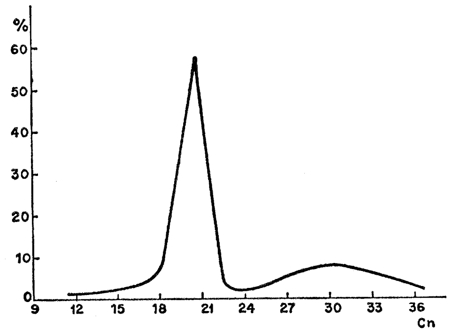

Fig. 1. Distribution of the *n*-alkanes with a carbon number greater than C_{14}. The total amount of this fraction was about 2 mg.

A factor that may be significant in the generation of petroleum is the presence of water. In order to gain an idea of its possible effect, we heated the behenic acid and the bentonite clay in a sealed tube with enough water to ensure its presence as a liquid at 200°C. In the low-molecular-weight fraction resulting from the reaction mixture, only very small quantities of the hydrocarbons from C_1 up to C_6 were detected, whereas in the higher molecular-weight fraction the *n*-alkanes up to C_{20} were detected. These experiments with and without water revealed a marked difference in the ratio of the various components to one another. This difference was the most striking with respect to the normal and branched chain C_4 and C_5 hydrocarbons. In the experiments with water the ratio was about 0.1, whereas in the experiments without water this ratio was about 4. The same figures were obtained for the ratio of iso- to normal-pentane. We have tentatively concluded that, because isomerization is very strong in the experiments without water, carbonium ions are the intermediates (*4*). Since isomerization is much less pronounced in the experiments with water, it is possible that radicals (*5*) act as intermediates in this case.

The behenic acid did not yield hydrocarbons after heating at 200°C without the bentonite clay. The bentonite contained only about 0.1 percent of organic carbon, but a blank run with it yielded only negligible quantities of hydrocarbons.

We fully realize that the conditions and the substances are quite different from those occurring in sediments. The results suggest that in the study of the processes of oil generation it should be realized that the presence of water may influence the mechanism by which the hydrocarbons are produced and that *n*-alkanes are not solely produced by the decarboxylation of fatty acids.

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Garnet Ratios and Provenance in The Glacial Drift of Western New York

Abstract. *The ratio of purple to red garnet identifies drift provenance. Low ratios indicate glacier flow from the central Adirondacks. Ratios of 1.4 or greater indicate flow from Canada, by way of the St. Lawrence lowland. The heavy mineral assemblages were evidently undiluted by local sources in western New York.*

The heavy minerals in tills of Ontario and adjacent areas have been studied (*1*). The results indicate that heavy minerals give evidence of the source of the glaciers that deposited the tills. Dreimanis and Terasmae (*2*), Dreimanis (*3*), and Connally (*4*) extended this work in Ontario and into western New York State. I published a complete list of heavy minerals in the drift of western New York in 1960. More recently Sitler (*5*) published a similar list for northwestern Pennsylvania and northeastern Ohio. However, Connally (*6*) has subsequently found garnet more useful than other heavy minerals for distinguishing drift units.

During 1960 and 1961, in conjunction with mapping the glacial geology of the western Finger Lakes region (*7*), I collected samples of both stratified drift and till in western New York from the Olean, Almond, and Valley Heads drift (Fig. 1). Samples were disaggregated and sieved. Heavy mineral grains in the size range between 0.062 and 0.350 mm were separated by use of bromoform, according to the standard procedure of Krumbein and Pettijohn (*8*). The heavy minerals were mounted in Canada balsam, and the grains were counted with a petrographic microscope.

The two categories with which this report is concerned are red garnet and purple garnet. "Purple garnet" includes both purple and colorless garnet, whereas "red garnet" includes both red and pink varieties. A ratio of purple garnet to red garnet (purple/red) was established for each locality sampled, according to the procedure of Dreimanis *et al.* (*1*). These ratios are illustrated in Fig. 1, and their distribution permits the map to be divided into two areas. North of the Almond moraine in the west, and north of the Valley Heads moraine in the east where the Valley Heads glacier evidently overrode the Almond deposits, purple garnet is clearly dominant. The ratios are almost all 1.4 or greater. The drift of this area is termed purple-garnet drift.

South of the Almond or Valley Heads moraine, all but three of the ratios are 1.2 or less. This is the area of Olean drift, termed mixed-garnet drift in this report. Four exceptions (underlined) are north of the Almond-Valley Heads border. These were identified as Olean drift in the field, and are so grouped for statistical analysis.

As a check on the observed data, the 90 percent confidence interval was calculated for the mixed-garnet and purple-garnet population means. The confidence coefficient indicates the degree of belief that the interval contains the population mean. The confidence interval for mixed-garnet drift is between 0.93 and 1.41 and was calculated from 15 samples. The confidence interval for purple-garnet drift is between 1.44 and 1.66 and was calculated from 37 samples. The lack of overlap between these confidence intervals suggests that there is a real difference between these garnet populations and therefore a difference in provenance for the two drift units.

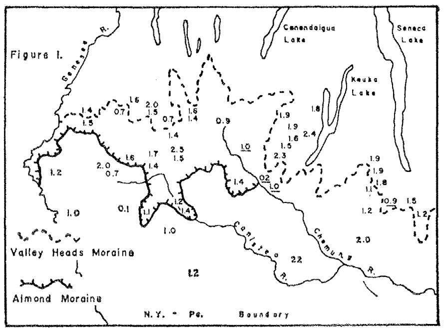

Fig. 1. Garnet ratios (purple/red) in the drift of the western Finger Lakes region, New York.

Dreimanis (*3*) demonstrated two possible source areas for purple-garnet drift and three for mixed-garnet drift. Connally (*6*) has shown that the purple-garnet drift probably had its source north of Montreal while the mixed-garnet drift probably originated in the north and central Adirondacks.

Dreimanis (*3*) suggested probable flow lines for purple-garnet and mixed-garnet drift in Ontario and New York. These flow lines are supported by the present study, as well as by topographic evidence described elsewhere (*6, 9*) and a study by Moss and Ritter (*10*). Ice depositing purple-garnet drift flowed into the Lake Ontario depression from the St. Lawrence lowland and was then diverted southward. Thus the glacier traversed the Paleozoic beds of western New York, perpendicular to their strike. In the area of mixed-garnet drift the glacier is presumed to have traveled southwest, subparallel to the regional strike of the Devonian strata.

Two of the three exceptional ratios in the mixed-garnet drift area are located in the southeast corner of Fig. 1. These localities show a dominance of purple garnet. Dreimanis's (*3*) report of similar ratios in samples from this area suggests to me flow from the southern Adirondacks for the eastern deposits of Olean drift. The third exception is located in the western part of the map. It is unexplainable at present and is treated as a random variation.

The question naturally arises whether the observed heavy mineral assemblages show significant dilution by sources in the Paleozoic sedimentary rocks. The major sources for sand-sized grains are the Silurian Grimsby sandstone adjacent to Lake Ontario and the Middle and Upper Devonian clastic strata of the northern Appalachian Plateau. Hoyt (*11*) reported that the dominant non-opaque heavy minerals in the Grimsby are tourmaline and zircon. Manley (*12*) reported similar results for the clastics of the Devonian sequence in central New York. Thus, if the garnet assemblages were enriched, tourmaline and zircon would have been added in even greater abundance. Tourmaline and zircon are only trace minerals (*4*) in both mixed- and purple-garnet assemblages; therefore I believe that dilution was insignificant.

During deposition of Olean drift,