

BITUMEN FROM THORNTON QUARRY

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ABSTRACT

Natural tar or bitumen occurs in small amounts in the Niagara dolomite that underlies northeastern Illinois. A sample from Thornton Quarry was compared with bitumen from Green River shale of Colorado, which has been intensively studied. It contains less nitrogen, about the same oxygen, and five times as much sulfur.

Thornton bitumen consists of 18% oils fraction, 48% resins, and 34% asphaltenes. Temperature-programmed gas chromatography of the oils fraction showed no n-alkanes, prominent triterpanes, and different proportions of steranes than in Green River bitumen. Other techniques with larger amounts of bitumen will be needed to characterize the resins and asphaltenes.

INTRODUCTION

Underneath the glacial clay of northeastern Illinois lie several hundred feet of Niagara limestone, deposited during Silurian times. Where reefs then grew, rounded hillocks of the ancient dolomite now protrude through the clay to provide access to samples of things that lived more than 400 million years ago. The rock itself is a mass of fossils ranging from one-celled sediments through shells to plant and animal skeletons.

Mixed in with the white dolomite are shiny black particles of bitumen that can be picked out of the rock or extracted from it with organic solvents. This bitumen is also a fossil but it has not previously been studied. At Thornton Reef, just south of Chicago, the bitumen is exposed by quarrying. It is so well distributed in pores and crevices that it seems to have been formed simultaneously with the rock, and it may also be of Silurian age. Figure 1 is a historical photograph of a pocket of bitumen from Thornton Quarry taken from the popular booklet by Dr. J. Harlan Bretz (1953) on the geology of the Chicago region.

We have compared Thornton bitumen with several familiar bitumens in various respects (Marschner 1973). At 25^o, it has a specific gravity of 0.068 and a viscosity of 7.2 log poises, values that are larger than those of typical natural tars or petroleum residues. Also, the specific gravity at a given viscosity is higher than other bitumens, suggesting that its composition is distinguishably different.

ANALYSES OF BITUMENS

Elemental analyses confirm an unusual composition. Table I compares Thornton bitumen with a natural bitumen from Green River shale of Colorado, which is of Eocene age and much younger than Thornton Reef. Because the kerogen in that shale is a likely future source for liquid fuels, its bitumen has been repeatedly studied. Thornton bitumen has about 6% sulfur, which is five times as much as Green River, but only 0.6% nitrogen, which is barely half as much. Both are high in oxygen content; as estimated by difference, Green River has about 6% and Thornton has 4 to 8%.

Bitumens contain a minimum of three distinguishable components: liquid hydrocarbon oils with less than 50 carbon atoms, viscous polycyclic resins with heterocyclic as well as arene rings and averaging perhaps 50 carbon atoms, and solid asphaltenes with 100 or more carbon atoms in the molecule. Resins usually predominate and act as solvent for the other components, the dissolved liquid oils thinning the solution, and the dissolved solid asphaltenes thickening it (Evans 1971).

The three components were determined by a standardized liquid-phase chromatographic procedure using silica gel as adsorbent and n-hexane as eluant (Duffy 1971). Table II presents values for three samples of Thornton bitumen that average about 17% oils, 46% resins, and 33% asphaltenes. The averages total only 96% because a small amount of finely divided minerals remains dispersed in the bitumen; for this reason, compositions are given both as actually determined and as adjusted to 100.0% bitumen. A Green River shale extract, analyzed by the same method, was richer in resins and poorer in asphaltenes. Analyses from the literature were obtained by other methods and are not comparable.

Once the bitumen had been separated into components, mass spectrometry was applied to begin to identify the constituents. Nonvolatility prevents obtaining a conventional mass spectrum of the asphaltenes, and lack of background prohibits interpreting the spectrum that can be obtained for the resins, but experience with petroleum permits resolution of the complex spectrum shown by the hydrocarbon oils. Table III presents the composition of the oils from Thornton bitumen as computed from the mass spectrum, using recently improved programs (Robinson 1971). Hydrocarbons with no rings are absent, in distinct contrast to petroleum residues, in which chain hydrocarbons ordinarily predominate. Arenes with as many as four or five rings, and cycloalkanes with as many as six rings occur, intermediate hydrocarbons with a total of three rings being

most abundant. Although some thiophenes were present in the oils fraction, most of the heterocyclic compounds would be expected to occur in the resins and asphaltenes fractions.

GAS CHROMATOGRAMS OF THORNTON BITUMEN

Bitumen extracted from Thornton dolomite provided the interesting chromatogram shown in Figure 2. It was obtained in a Hewlett-Packard 5750 research chromatograph temperature-programmed to 400° at a rate of 10° per minute. The dual columns were 6-meter lengths of 3-millimeter tubing, packed with 3% OV-1 on Chromosorb G-HP. Each column was provided with a hydrogen-flame ionization detector, the nonsample contribution of the idle column being subtracted from the total contribution of the active column to provide a sample chromatogram corrected for extraneous ionization. In obtaining this and subsequent chromatograms, a crude-oil standard was run daily to establish a n-alkane scale by which to express the positions of other substances.

The chromatogram shows a dozen or so prominent peaks that are numbered in the figure, plus at least another sixty smaller ones. Major ones extend from below twenty to above forty carbon atoms, and hence represent oil constituents primarily, but are superimposed on a rising curve that represents an unresolved background of resin constituents. Asphaltenes and any minerals remain on the packing at the front of the column and do not contribute to the pattern. Peaks are irregularly spaced and clearly do not correspond to the successive n-alkanes that dominate chromatograms for typical crude petroleum. The most prominent peaks fall in the same range as n-alkanes with 29 to 38 carbons, which is probably equivalent to 30 to 40 actual carbons, and some are sharp enough to represent individual compounds.

Another chromatogram for native Thornton bitumen picked directly from the rock rather than extracted from it is shown in Figure 3. Columns only two meters long were used, and separation was consequently not as good, but the pattern is almost the same.

In an attempt to concentrate any n-alkanes that might be present, some of the native bitumen was "dewaxed" with methylethyl ketone to give the two fractions, one "soluble" and one "insoluble," that are compared in Figure 3. Some separation had occurred, as the ratio of oils below 40 carbons to resins above 40 carbons was lower in the "insoluble" fraction. But both compositions are otherwise indistinguishable from that of the original bitumen; evidently no n-alkanes are present.

GAS CHROMATOGRAMS OF OILS FRACTION

Most of the character visible in total Thornton bitumen can be seen in gas chromatograms of the oils fraction alone. An oils fraction from Table II, given as the top curve in Figure 4, presents a pattern intermediate in sharpness between Figures 2 and 3, which it matches peak-for-peak within 0.2 carbon. In the absence of resins, however, the general trend is down rather than up, indicating a decrease in the amount of oils fraction with carbon number.

Furthermore, most of the character of the oils fraction is concentrated at the front or least-sorbed end. n-Hexane eluate from the analysis column was collected in four successive lots representing 0 to 32% (A), 32 to 65% (B), 65 to 85% (C), and 85 to 100% (D) of the oils fraction. Gas-chromatographic patterns of the separate lots, aligned with the aid of n-docosane added as an internal standard, appear below that of the total oils in Figure 4.

Lot A so closely resembles the total oils that only three prominent peaks are obviously depleted: 29.8, 36.2, and 38.7. Several pairs show up almost unchanged, notably 33.7-34.3 and 37.5-38.0. So many other major and minor peaks match in all ranges of the two curves that the exceptions are easy to identify.

Lot B retains much of the pattern of Lot A, indicative of considerable overlap, but other substances are also present. Noteworthy is a large peak at 29.8 that was depleted in A, and traces of which are visible in curves A and C. Because Lots A and B together comprise 65% of the oils fraction, dominance of the bitumen pattern by the compounds responsible for the major peaks of Lot A is understandable.

Lot C overlaps B on one side and D on the other. Its major constituents are 29.4 and 31.2, which were hidden by the taller peaks at 29.8 and 31.8 in Lot A, and especially the quartet of 36.2, 37.1, 37.8 and 38.4. Three of these were visible in the spectra of the original bitumen, whereas 37.8 was hidden by the tall peaks at 37.5 and 38.0 in Lot A.

Lot D is the last of the oils to elute before the resins, and is richest in the arene rings previously indicated in Table III. Its most prominent peaks fall at regular intervals that correspond to 31 to 37 n-alkane carbons, apparently with an even-number predominance. These constituents are not n-alkanes, which would desorb much earlier than adjacent to the resins, but are probably some other homologous series. The few minor peaks visible in D can be accounted for by overlap with Lot C.

Relations worked out between the lots and the total oils in Figure 4 have been successfully applied to the previous figures. With the possible exceptions of a few small peaks, the entire pattern of Figure 3, for example, can be accounted for by constituents visible in the patterns of the four lots.

INTERPRETATION OF GAS CHROMATOGRAMS

Clues to the nature of the hydrocarbons present are contributed by work done elsewhere on the composition of bitumen from Green River shale. Especially helpful are two parallel studies: Anders and Robinson (1971) of the Bureau of Mines at Laramie, Wyoming, who worked with a sample from the "Demonstration Mine near Rifle" freed successively of asphaltenes, arenes, and n-alkanes; and Callegos (1971) of the Chevron Research Company at Richmond, California, who worked with a sample from

the "vicinity of Grand Valley" isolated by four elutions from alumina with cyclohexane. Both used a combination of separation by gas chromatograph and identification by mass spectrometer to achieve a semi-quantitative analysis of the many constituents found in or indicated by extensive previous work.

Despite differences in original shales and methods of processing the bitumens, the two gas chromatograms were similar, as shown in Figure 5. Both segregated seven major peaks, presumably the same ones, and 50 to 70 lesser ones--a complexity comparable to that of Thornton bitumen. Prominent in both studies are a series of noncyclic isopranes just below twenty carbon atoms, especially the pristane and phytane that are often found in petroleum, a group of steranes and pentacyclic triterpanes with about thirty carbons, and a lone last peak for carotane with forty carbons.

There is little superficial resemblance to Thornton bitumen, in which isopranes below 20 are absent and the first major peaks occur at 23.2 and 25.9 carbon atoms. The range of peaks that appear thereafter from 29.8 to 36.2 could represent polycyclic hydrocarbons similar to those in Green River shales, but the proportions must be entirely different. The last major peak at 38.7 has the position of carotane, but the larger twin peaks at 37.5 and 38.0 have no counterpart in the shale. The two bitumens certainly have distinguishable profiles.

CONCLUSION

Nevertheless, the similarities between Thornton and Green River bitumens in the intermediate range of steranes and triterpanes are too close to dismiss. Some of the Thornton peaks near 30 carbon atoms may represent steranes--perhaps the same cholestane, ergostane, and sitostane that occur in Green River bitumen. Such a compact series of steranes must have been formed in sequence, either by selective synthesis from smaller molecules, or by selective degradation of larger ones. This series in varying amount may occur generally in bitumens of various ages.

In a parallel way, the Thornton peaks between 32 and 36 carbon atoms may represent triterpanes, perhaps even including the gammacerane and hopane that occur in Green River bitumen. But such specific structures may be synthesized only by particular families of living matter and hence contributed by them to only an occasional bitumen. Finally, carotane, the reduction product of the carotenes that are widely responsible for yellow colors in plants, may be either present in or absent from whole classes of bitumens, depending upon circumstances of source or environment.

Further work on Thornton bitumen may uncover clues as to its age and source. Whether compounds not now found were ever present and when the compounds found were actually formed are questions that can only be speculated upon. But some life patterns common in the Eocene did not even exist in the Silurian, and survival from Silurian times would have required greater resistance than survival from Eocene times, only a tenth as long ago. Identification of any unique structures in Thornton bitumen could be extremely helpful.

Further study of these "biological markers" involves geology and chemistry as well as biology to pose a fascinating if complicated interdisciplinary problem. In the chemistry area, examination of larger amounts of bitumen would permit techniques that could bring better separations into play. Successive molecular distillates with 20-odd, 30-odd, and 40-odd carbon atoms have already been successfully collected. Such clean cuts should yield especially well to fractionation by adsorption, and varieties of extraction, adduction, and diffusion techniques are available for further separation. Thereafter, the mass spectra of increments from a gas chromatograph should go far to distinguish what species are present.

Especially interesting and significant because of their abundance are the resins. Their gas-chromatograph pattern shows little character in contrast to that of the oils fraction; either the composition is more complicated or the constituents are more difficult to distinguish. The resins have not yielded to methods that are conventional for separating the relatively saturated constituents of the oils fraction. Other techniques may prove more successful, but new methods may yet have to be devised.

ACKNOWLEDGEMENTS

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Table I - Elemental Analyses of Bitumens

	Weight Percent				
	<u>carbon</u>	<u>hydro- gen</u>	<u>sulfur</u>	<u>nitro- gen</u>	<u>oxygen + errors</u>
	* <u>from Thornton dolomite</u>				
original bitumen	74.9	10.4	6.3	0.6	7.8
16% oils	77.4	11.9	2.1	0.0	8.6
51% resins	81.2	9.7	5.2	0.4	3.5
33% asphaltenes	79.6	7.4	8.1	1.2	3.7
100% (calculated)	80.1	9.3	5.7	0.6	4.3
	<u>from Green River shale</u>				
total organic matter	80.5	10.3	1.0	2.3	5.9
extracted bitumen	81.3	10.9	1.0	1.0	5.7
literature (Robinson 1960)	80.4	11.1	1.1	0.9	6.5

* by difference

Table II - Component Analyses of Bitumens

weight percent (values in parentheses are for mineral-free bitumen)

<u>Thornton bitumens</u>						
oils	14.9	(15.6)	18.5	(18.9)	17.7	(18.4)
resins	49.4	(51.6)	46.0	(47.2)	45.4	(47.0)
asphaltenes	<u>31.4</u>	<u>(32.8)</u>	<u>33.1</u>	<u>(33.9)</u>	<u>33.3</u>	<u>(34.6)</u>
total	95.7	(100.0)	97.6	(100.0)	96.4	(100.0)
<u>Green River shale extracts</u>						
oils	19.0	(21.1)	25.0	(25.3)	--	(14.8)
resins	66.7	(73.9)	38.0	(38.4)	--	(67.2)
asphaltenes	<u>4.5</u>	<u>(5.0)</u>	<u>36.0</u>	<u>(36.3)</u>	--	<u>(18.0)</u>
total	90.2	(100.0)	99.0	(100.0)	--	(100.0)
			Robinson 1960		Robinson 1967	

Table III - Mass Spectral Analysis of Oils Fraction
Weight Percent

number of cycloalkane rings	number of arene rings					<u>total</u>
	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4 or 5</u>	
0	0.0	2.6	1.0	5.7	2.8	12.1
1	13.7	4.8	3.6	2.1		24.2
2	13.1	7.0	2.9			23.0
3	17.5	3.2	2.0			22.7
4	3.4	2.0				5.4
5	4.0					4.0
6	2.0					2.0
total	53.7	19.6	9.5	7.8	2.8	93.4*

* balance of 6.6% is thiophenes

THORNTON BITUMEN



Figure 1

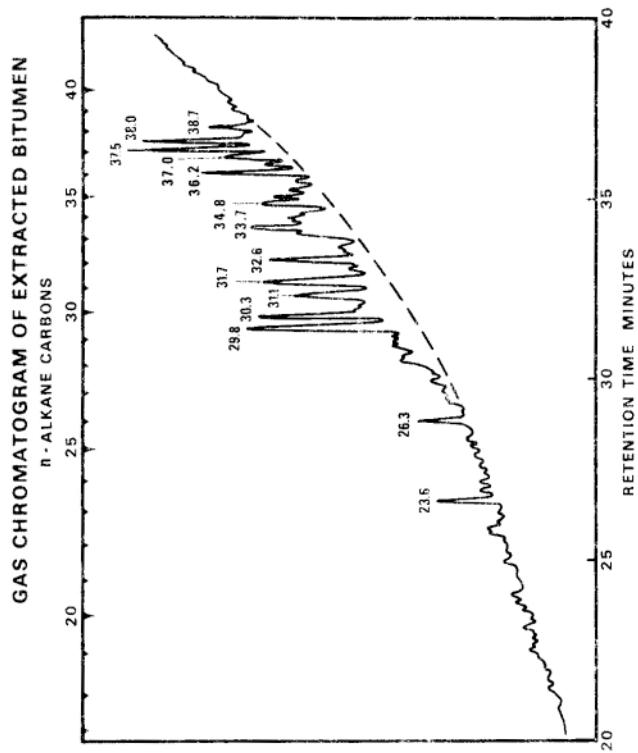
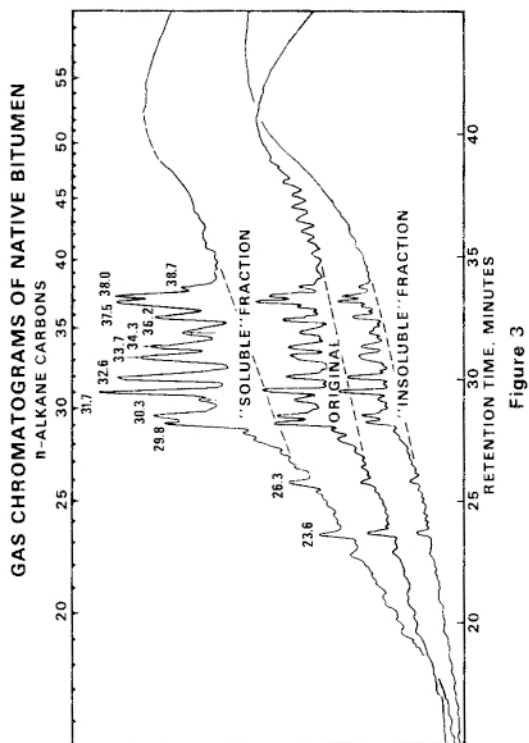


Figure 2



GAS CHROMATOGRAMS OF FRACTIONS OF SATURATES
n-ALKANE CARBONS

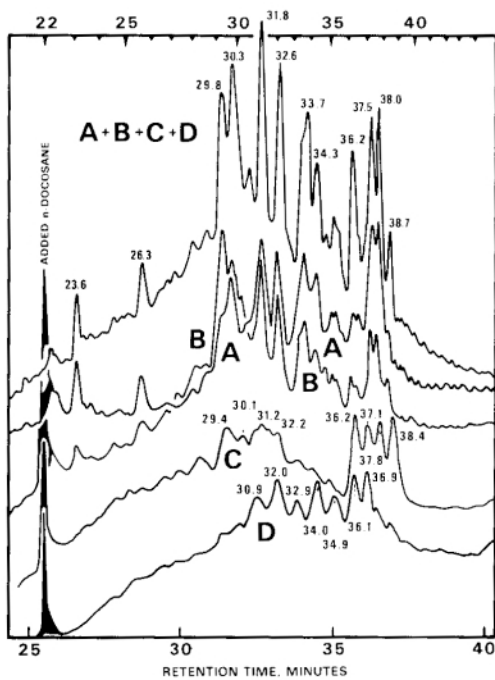


Figure 4

