Kerogen in the Chattanooga Shale

Study of its origin and composition suggests why these shales are not source beds for petroleum.

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Abstract. The Chattanooga shale contains insoluble organic matter (kerogen) derived from terrestrial (humic) and from marine (sapropelic) sources. Kerogen from sapropelic sources contains more hydrogen than kerogen from humic sources. Thus the hydrogen content of the sapropelic contribution, and of the kerogen, increases toward that part of a shale most likely to be a source bed for petroleum. Uranium in the shale is derived from the adjoining land mass.

Several excellent reports on the geology of the Chattanooga shale have been published recently by Brown (*1*), Glover (*2*), and Conant and Swanson (*3*). A number of concerted attempts have also been made to attain an understanding of the interrelations between the organic constituents, the distribution of uranium, and the pyrolytic oil yield of the shale (*4*). No satisfactory integrated explanation has as yet been offered, however, for the various geological and geochemical processes that occurred during deposition of the mud and during its dehydration and compaction to form the shale. Moreover, no explanation has been presented for the lack of appreciable quantities of crude oil associated with the Chattanooga shale, which, being of marine origin and having as much as about 25 percent of organic matter, has a number of attributes normally ascribed to source beds for petroleum. Geochemists have long been concerned with this particular problem, as it is intimately related to the recognition of petroleum source beds, to the origin of petroleum, and thus to the search for crude oil. The study reported briefly here suggests answers to these questions, based on considerations that are useful for geochemical studies of marine shales other than the Chattanooga, as well as for rapid evaluation of these shales, in whole or in part, as petroleum source beds.

In 1960, Breger, Tourtelot, and Chandler reported their study of the organic matter isolated from samples of the Sharon Springs member of the Pierre shale (*5*). In that work, the ground shale samples were preextracted with chloroform and 1:1 benzene-alcohol, and the residual shale was then treated with hydrochloric and hydrofluoric acids under mild conditions to isolate the organic matter, which is insoluble in the organic solvents and which is normally called "kerogen" (*6*). The kerogen so isolated still contained pyrite or marcasite, or both, but was free of clay minerals and other silicates as far as could be determined by x-ray analysis. Kerogen, isolated in similar fashion from samples of Chattanooga shale, when retorted, yields pyrolytic oil. Interpretation of the analyses (*7*) of the kerogen isolates was based on the following considerations:

1) Organic matter in the Pierre and Chattanooga seas was derived both from terrestrial sources (humic material) and from aquatic sources (sapropelic material). The insoluble organic complex (kerogen) of each of the shales is, therefore, composed of variable contributions from both terrestrial and aquatic sources. The relative contributions to a carbonaceous shale of these two types of substances have been suggested by other workers (*8*).

2) Sapropelic material normally has a higher hydrogen content than humic material. Thus, boghead coal, of algal origin, may contain 10 to 12 percent hydrogen (*8*), whereas comparable coals derived from terrestrial humic material normally contain about 5.5 percent hydrogen. The hydrogen content of coals does not vary significantly with increase in rank until the bituminous range is reached. Because this hydrogen value is constant, it can be used as an index to determine the relative contribution of terrestrial organic material to a shale, as shown later in this report.

3) In comparing the compositions of a suite or organic isolates from a shale, such as Pierre or Chattanooga, increase in hydrogen values can be correlated with increase in the proportion of sapropelic constituents and with increase in the distance from the paleo-shoreline.

On the basis of these three considerations, increases in hydrogen values of organic isolates from the Pierre shale were correlated with distance from the shoreline. The same approach has been used in the study of the Chattanooga shale, where hydrogen as a geochemical indicator has been tested with 22 samples from eight localities (Fig. 1). Most of the samples were from the upper or Gassaway member of the Chattanooga shale, but a smaller number were from the lower or Dowelltown member.

Conclusions

On the basis of interpretation of the hydrogen values and other data (Table 1), the following conclusions have been drawn with regard to the Chattanooga shale:

1) Hydrogen values for organic isolates from the Dowelltown member appear to be generally higher than those for the overlying Gassaway member of the shale. It is therefore concluded that the contribution of humic material of terrestrial origin to the total organic matter of the sediments was lower during Dowelltown time than during Gassaway time.

2) Hydrogen values of the organic isolates are unusually low for samples from the southeastern part of the major shale body near the Walden Ridge area (localities C48 and C49) and in Alabama (locality C64). Low hydrogen values, as had also been noted for the Pierre shale, are taken as evidence that the organic matter, at the time of deposition, was under relatively shallow water, where it was subjected to an oxidizing environment. Low hydrogen values, therefore, indicate that the sediment was deposited close to a shoreline (Fig. 1).

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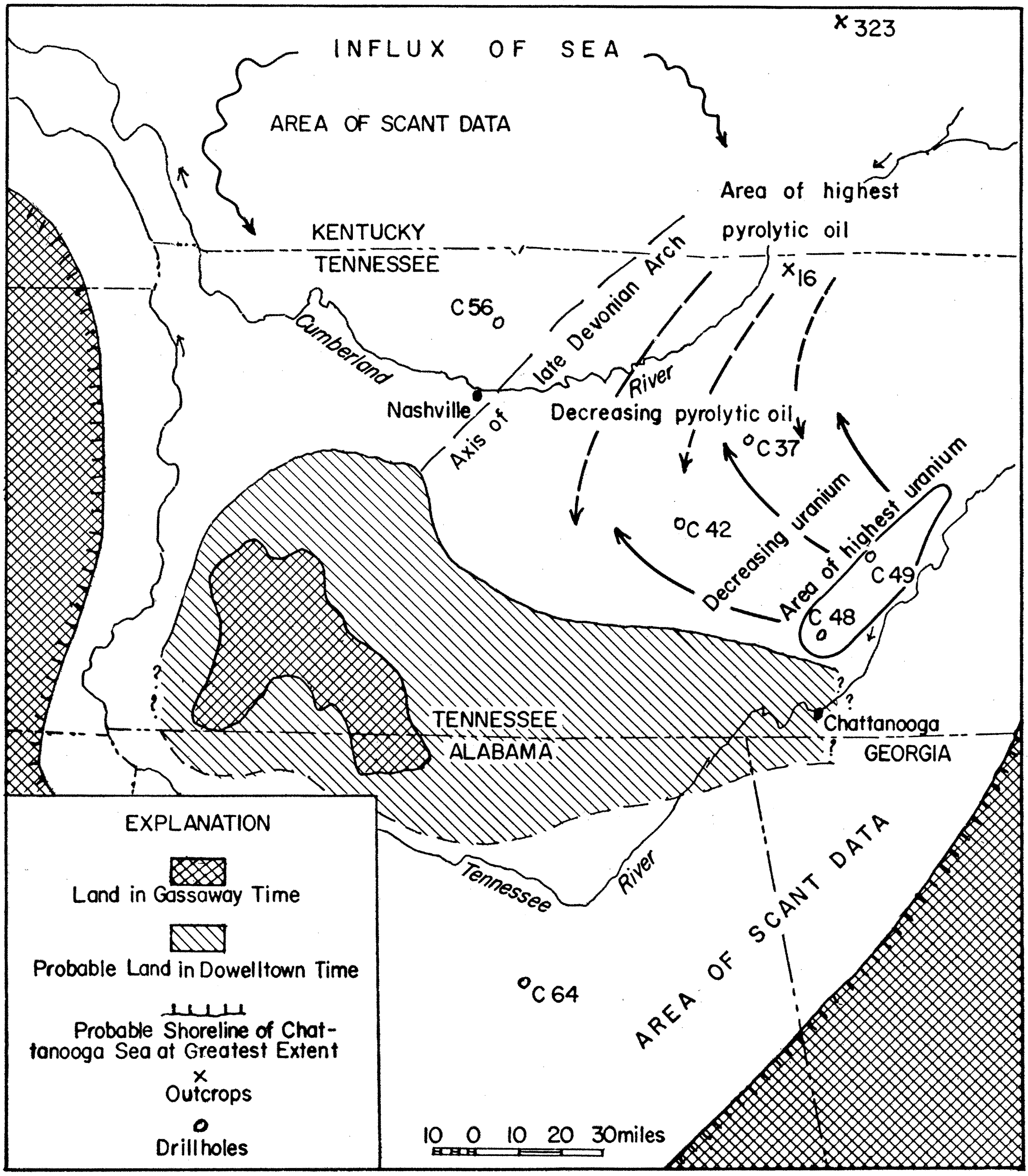

Fig. 1. Sketch map showing an interpretation of late Devonian paleogeography in central Tennessee and adjoining states.

3) Pyrolytic oil yield cannot be correlated with total organic matter for the Gassaway member—a finding which illustrates that pyrolytic oil is dependent upon the type of organic matter present (Fig. 2). Some degree of correlation does appear for the Dowelltown member, where there seems to have been, as already noted, a higher proportion of sapropelic material in the sediment. Development of an index by which the proportions of sapropelic and humic materials could be established for a series of kerogen isolates would permit reevaluation of the pyrolytic oil-kerogen correlation.

4) The major source of uranium was to the southeast of the Chattanooga Sea, probably in what is now western North Carolina and northern Georgia and Alabama. High uranium values in the Walden Ridge area (about 70 parts per million) decrease in a northwesterly direction to about 60 parts per million as the distance from the shoreline increases (Fig. 1). Had the uranium originated in the sea, the uranium content of the shale would have been greatest in the Northern Highland Rim (localities C56 and 16), where the Chattanooga Sea is thought to have entered the Tennessee embayment, and would have been least in the Walden Ridge area, which was

near the farthest limit of the sea. The opposite is the case.

5) The percentage of organic matter is linearly related to the uranium content in the shale, demonstrating that the type of organic matter is not important in the fixation of uranium (Fig. 3). Both sapropelic and humic substances are acidic and are able to fix uranium in the form of the uranyl ion, which can later be reduced to uraninite (*9*). Evidence has been obtained that the uranium in the shale exists as a phase separate from the organic and inorganic constituents, probably as uraninite (*10*).

In addition to providing a basis for these specific conclusions, evaluation of the origin and composition of the kerogen isolates from the Pierre and Chattanooga shales has demonstrated why these shales are not source beds for petroleum in spite of a number of attributes which suggest that they might be. Terrestrial humic material, which is related to coal, has been widely disseminated over tremendous areas in marine seas; sapropelic material of marine origin, which is apparently the source material for petroleum, is present in these sediments in amounts too small for conversion to significant quantities of crude oil.

Table 1. Data on oil yield and uranium content of samples of Chattanooga shale in Tennessee and adjoining states. For localities, see Fig. 1.

Locality and sample No.	Member and unit*	Thickness of sample (ft)	Organic isolate in shale (%)	Hydrogen in organic isolates (moisture and ash free) (%)	Oil yield of shale (gal/ton)	Uranium in shale (parts per million)
323-A	Gz	5.00	21.6	6.2	10.5	36
323-B	Gz	12.00	16.7	6.1	6.2	39
323-C	Gz	13.00	15.3	5.9	3.8	37
C56-A	Gz	9.67	26.3	5.5	7.6	56
C56-B	Dz	13.15	10.2	6.7	6.5	9
16-A	Gz	6.00	18.6	5.4	7.0	46
16-B	Gz	5.50	18.3	5.2	8.5	52
16-C	Gz	5.15	24.2	4.9	6.3	59
C37-2	Gu	6.80	29.3	5.5	8.6	86
C37-3	Gm	3.01	13.0	5.1	3.8	33
C37-4	Gl	7.62	23.8	5.6	10.2	57
C37-5	Du	11.50	5.9	6.3	2.6	12
C37-6	Dl	5.11	17.3	6.4	7.6	34
C42-2	Gu	6.50	28.6	4.9	4.5	80
C42-3	Gm	1.86	15.9	4.9	4.0	49
C42-4	Gl	9.99	20.4	5.3	5.2	52
C49-31†	Gu	5.40	26.0	4.0	5.3	92
C49-33	Gl	2.85	20.0	4.4	2.8	63
C49-41	Du	6.46	8.3	4.3	Trace	11
C48-A	Gz	15.07	23.3	3.8	0.7	69
C64-A	Gz	11.95	16.7	3.9	0.7	44
C64-B	Du	7.40	8.4	4.1	1.2	19

* *Gz*, Undivided Gassaway member; *Gu*, upper unit, Gassaway member; *Gm*, middle unit, Gassaway member; *Gl*, lower unit, Gassaway member; *Dz*, undivided Dowelltown member; *Du*, upper unit, Dowelltown member; *Dl*, lower unit, Dowelltown member. † Incomplete section analyzed.

The foregoing considerations indicate that a potential petroleum source bed can be evaluated only on a relative basis; the oil-forming potential is dependent upon the sapropelic contribution to the original sediment. Thus, analysis of a series of samples from a particular shale body may not tell, with the indices now available, whether a shale is a potential source bed, but it will point, on the basis of increasing hydrogen values, toward those parts of the shale that are the most likely source beds, if any exist.

On the assumption that crude oil formed in a source bed will migrate into the nearest trap, the use of hydrogen values as indices to establish the

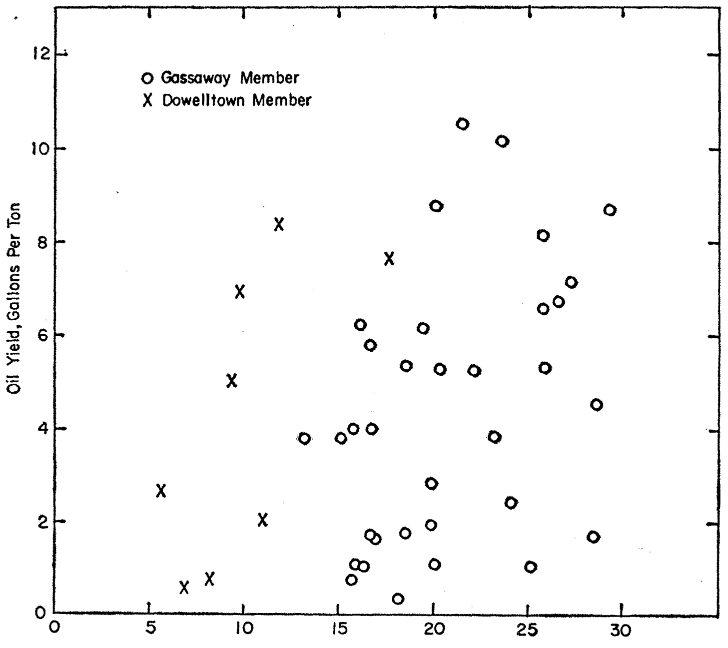

Fig. 2 (above). Relationship of total organic isolate to pyrolytic oil yield for Chattanooga shale. Data for 43 analyses.

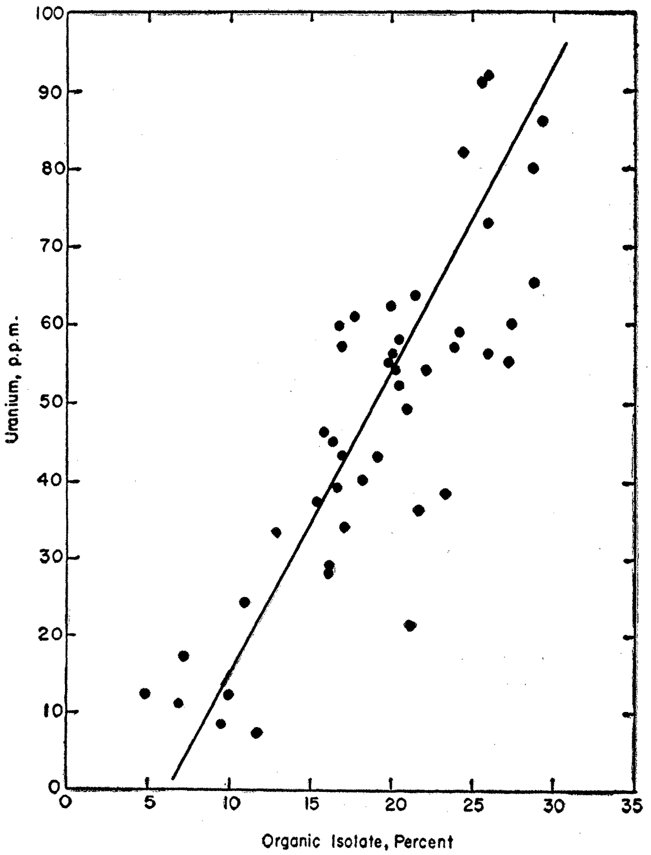

Fig. 3 (right). Relationship of total organic isolate to uranium in the Chattanooga shale. Data for 45 analyses.

maximum contribution of sapropelic material to a potential source bed may simplify the search for oil by ruling out parts of a formation and pointing to the potential source beds in a basin of deposition.

Inasmuch as the Chattanooga and Pierre shales contain kerogen that is primarily of humic (terrestrial) origin, they should, in spite of the fact that they are marine, be considered coaly shales (*11*).

References and Notes

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7. The shale isolates were prepared by Sarah Berthold and the uranium analyses were made by members of the analytical staff of the U.S. Geological Survey. Proximate and ultimate analyses of the shale isolates were carried out by the U.S. Bureau of Mines, Coal Analysis Laboratory, Pittsburgh, Pa. We are particularly indebted to Roy Abernethy and Forrest Walker, without whose cooperation and assistance this work might not have been possible. All analyses were submitted in routine fashion to eliminate any possible bias in the results.
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Chemical Control of Water Loss in Growing Plants

Abstract. Immersing the roots of growing strawberry plants in aqueous solutions of 8-hydroxyquinoline sulfate closes the stomata, reduces water loss, and increases the time before complete wilting under drought conditions. Under such drought conditions plant survival and vigor are increased. Prolonged closing of the stomata seems to be the principal mode of action of the chemical.

This study verifies observations made over a period of years that 8-hydroxyquinoline sulfate retards wilting in several species of plants. Zelitch (*1*) has shown that 8-hydroxyquinoline sulfate prevents closed stomata of tobacco leaves from opening under conditions favorable for the opening of stomata (*1*). Ferri and Levy have shown that an aqueous solution of β-naphthoxyacetic acid watered on the soil closes the stomata of nasturtium leaves (*2*).

Because most of the water loss from a plant is through the stomata, it was postulated that the reduction of water loss in plants treated with 8-hydroxyquinoline sulfate is due to the closing of the stomata by this material. Our experiment shows that this material closes open stomata and keeps them closed under conditions favorable for opening.

The roots of five growing strawberry plants with open stomata were immersed in tap water, and the roots of five others were immersed in aqueous solution of 8-hydroxyquinoline sulfate (2000 ppm) for ½ hour. At the end of this period of time the stomata in a sample of five leaves from the plants immersed in water were still open. In a sample of five leaves from the plants immersed in the test solution the stomata were closed. A duplicate experiment in which the plant roots were immersed for 3 minutes gave identical results. The "open" or "closed" position of the stomata was determined by silicone-rubber impressions of the lower epidermis (*1*). The almost immediate closing of the stomata after immersion of the roots indicates a direct effect of 8-hydroxyquinoline sulfate on the stomata and not an indirect effect by action on the roots. We have observed immediate closing of the stomata of excised leaves of chrysanthemum where the cut end of the petiole was immersed in a test solution, indicating that the stomata are closed by direct action and that roots are not essential to the action.

We suggest that closed stomata are the chief factor for the reduced water loss shown in the following experiment. Young growing strawberry plants were removed from the soil, and their roots were washed clean with tap water. The roots of five plants were then immersed in tap water, and five each in 1000-ppm and 2000-ppm aqueous solutions of 8-hydroxyquinoline sulfate. After immersion, the roots were again washed thoroughly in tap water, and the plants were set in waterproof pots containing 350 g of dry sand. After planting, 150 ml of water was added to each pot, and the pots were weighed. No more water was added during the experiment. The pots were reweighed 4, 6, 10, and 14 days later to determine water loss (Fig. 1). Fertility of the sand was low, and there was no growth of plants to offset loss in weight by transpiration and by evaporation of water from the uncovered surface of the sand.

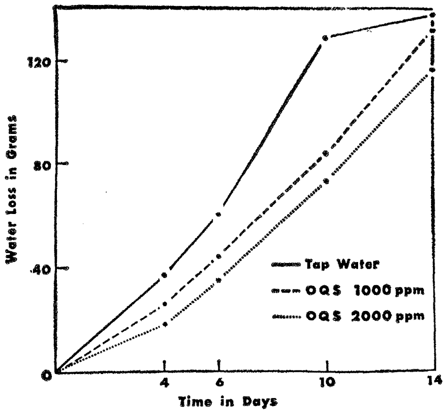

Fig. 1. Chemical reduction of water loss by treatment of roots for 30 minutes before planting. Water is lost from both pot and plant.

Up to the 14th day the plants soaked in water showed a greater water loss than those soaked in 8-hydroxyquinoline sulfate, and the plants soaked in 1000 ppm of the test solution showed a greater loss than those soaked in 2000 ppm. The greatest difference between treatments in water loss was during the first four days. On the 14th day four of the five control plants had completely wilted, with a consequent reduction in water loss. The treated plants continued to lose water at the former rate. The higher loss at the lower concentration can be accounted for by differential action of the two concentrations on the stomata, with the lower concentration allowing the opening of more stomata. The time to complete wilting was as follows: water, 11 days; 1000-ppm solution, 15.6 days; and 2000-ppm solution, 19.2 days. Similar experiments showed that these results were reproducible.

To determine whether the preplanting treatment would influence the survival of the plants once they had wilted, all the plants were rewatered 1 day after the last plant had wilted or 21 days after the start of the experiment. Within 2 days all five plants treated at a concentration of 2000 ppm had revived; 3 of the plants looked as if they had never wilted. Four plants treated at a concentration of 1000 ppm survived but were in poorer condition than those treated at a concentration of 2000 ppm, and one was barely alive. Only one plant that had been soaked in water survived, and it was barely alive. Thus