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## GEOCHEMICAL TRENDS IN CHESTERIAN (UPPER MISSISSIPPIAN) WALTERSBURG CRUDES OF THE ILLINOIS BASIN

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#### ABSTRACT

Twenty-five samples of Chesterian (Upper Mississiptian) Waltersburg crude oiland 11 core samples of Waltersburg shale were spectrochemically analyzed for trace concentrations of nickel and vanadium. In addition, concentrations of some of the light hydrocarbon components ( $\leq C_{29}$ ) were determined in 14 of the crude oil samples using gas chromatography.

Indirect evidence, based primarily on the relation between Waltersburg oil occurrence and faulting, suggests that these crudes came from older sediments. In contrast, strong regional trends, which parallel the primary sediment transport direction in the ancient basin, were found in the trace metal contents of these crudes. Almost random variations were found in the naphthene and aromatic contents of a series of crudes entrapped in isolated Waltersburg sand bodies in southeastern Illinois.

No regional trends were identified in the trace metal content of the shales. However, the concentration ratios of Ni/V in the shales were similar. In this respect, the trace metals in shales were like the trace metals in the crudes,

#### INTRODUCTION

In the past 20 years, new analytical techniques have made it possible to investigate in detail the composition and properties of crude oils and potential peroleum source materials (Hedberg, 1964). Measured variations in the properties of crude oils and their implied precursors have been interpreted in terms of original source materials, paleogeography, migration effects (both primary and secondary), and maturation of crudes in petroleum reservoirs after entrapment. As a result of these studies, new hypotheses have been formulated concerning the origin of petroleum and the mechanics of migration.

Recent studies of the Illinois Basin concerning the formation of brines (Graf, Meents, Fiedman, and Shimp, 1966; Clayton et al., 1966), hasin hydrodynamics (Bredehoft et al., 1963; Graf, Friedman, and Meents, 1965), and the possibility of deep production (Bell et al., 1964) have led to a revival of interest in the basic problems of Illinois oil geology. In other oil provinces, workers have found that variations in the chemical composition of crudes can be related to both basin paleogeography and the effects of crude migration.

Bonham (1956) showed that the concentrations of nickel and vanadium in Pennsylvanian crudes from the Seminole Basin in Oklahoma reflected the paleogeography of the basin. The concentrations of these trace metals were greatest in crudes found near the ancient shorelines, and their concentration decreased progressively basinward. Bonham did not state, however, whether or not these variations in concentration were inherited from the hydrocarbon source materials or were the result of basinward migration through the Pennsylvanian rocks. He reported concentrations of nickel that ranged from less than 0.1 ppm (parts per million) to 8,5 ppm and concentrations of vanadium that ranged from less than 0.1 ppm.

Silverman (1965) found that the concentration of paraffins in a series of related crudes increased as the concentration of vanadium porphyrins decreased, in an almost direct relation to the inferred distance that the crudes had migrated through the carrier bed. Hodgson and Baker (1959) showed evidence that "relocation" of crudes was effective in altering their trace metal content.

Witherspoon and Nagashima (1957) studied variations in concentration of nickel and vanadium in samples of Illinois crude oil from reservoirs that ranged in age from Devonian to Pennsylvanian. They reported a marked systematic reduction in the concentration of nickel and vanadium with increasing age of the reservoir rocks. Nickel varied in concentration from 0.5 ppm in Devonian oils to over 5 ppm in some basal Pennsylvanian oils. They also found that the nickel concentration in their samples was generally two to three times larger than the vanadium concentration.

This study presents variations in trace metal content (nickel and vanadium) and light hydrocarbon components of the crudes entrapped in the Chesterian (Upper Mississippian) Waltersburg Formation (fig. 1). These oils were chosen for study because maps of Waltersburg production showed long producing trends that were related to both sand development and faulting. Swann (1951) suggested that the Waltersburg oils had probably migrated upward through faults into the Waltersburg reservoirs. An attempt was made in this study to identify the effects of crude migration away from the faults through the formation. Samples of crude oil were collected at intervals of about 2 miles along two of the Waltersburg trends, which are labeled Trend I and Trend II in figure 2. Samples were obtained from a larger area in order to see if broad regional trace metal trends similar to those described by Bonham (1956) could be found.

Samples of shale from the Waltersburg were analyzed to see if any general relation could be found between the nickel and vanadium content of the shale and crude oil, or if geochemical evidence would support the geological conclusion that Waltersburg oils came from older sediments.



Figure 1 - Upper part of Mississippian stratigraphic column in the Illinois Basin (Swann, 1963).



Figure 2 - Oil production, sand development, and faulting in the Waltersburg Sandstone. there are some differences in the faults shown in figure 2 and



Fault data from Bristol (in press) were not available when figure 2 was constructed. Although those given by Bristol, these differences do not affect this paper.

#### GEOLOGIC SETTING

#### General

In the Illinois Basin, the Paleozoic sediments have a maximum thickness of about 14,000 feet and range in age from Crotkan (Upper Cambrian) to Pennsylvanian. As described by Swann and Bell (1958, p. 449), "The Illinois Basin has no mobile boundary, no border mountain belt. It is an area of gentle downwarping surrounded by broad regional domes or arches which have been only weakly positive."

The basin is bounded on the north by the Wisconsin, Kankakee, and Mississippi River Arches, on the east by the Cincinnati Arch, and on the west by the Ozark Dome. These features were all present by at least Champlainian (Middle Ordovician) time. Geologic evidence, primarily from isopach and facies maps, indicates that during Paleozoic time the basin was open toward the south. Uplift of the Pascola Arch, across southwestern Kentucky and Tennessee, closed the basin after Pennsylvanian deposition ended.

Uplift at the end of Mississippian time is shown by widespread truncation and channeling of the pre-Pennsylvanian sediments, Pennsylvanian sediments overlap progressively older sediments to the north, and thus Chesterian (Upper Mississippian) rocks outcrop only around the southern half of the Illinois Basin.

The Rough Creek Fault Zone and the Wabash Valley Fault Complex apparently developed after the end of Pennsylvanian deposition. Ross (1963) has shown that some of the faults have been recurrently active since that time.

#### Chesterian Deposition

Sediment deposition in the basin during Chesterian time was rhythmic (Swann, 1963). Units of sandstone and shale are separated by persistent units of limestone and shale (fig. 1). Twelve to fourteen major cycles of limestone and sandstone deposition are recognized; the total section reaches a maximum thickness of about 1500 feet near the outcrop in southern Illinois.

Shales make up approximately 50 percent and limestones 25 percent of the total Chesterian column (Swann and Bell, 1958). The limestones generally thicken to the south and southwest, and the mean cross-bedding direction, measured at sandstone outcrops, also is oriented toward the southwest (Potter et al., 1958). The sand bodies are quite variable in thickness and often have been described as channels. Almost all of the major elongate sand bodies are oriented parallel to depositional slope (Potter, 1962).

Generally, it is believed that a large river system carried reworked clastics into the basin from the northeast. When sediment input from the river system was large in comparison to basin subsidence, the river's delta complex prograded across the basin toward southwestern Illinois. Map patterns of the resulting sand bodies change progressively basinward from channel tributaries to delta distributaries to elongate and sometimes isolated marine sand bodies (Potter, 1962). Swann (1964) modified the above interpretation with the idea that the major sand bodies were deposited primarily in a near-shore marine environment as delta bar fingers. He considers the reworking of the bar fingers by streams and tidal action as being secondary in importance in terms of total sand deposition.

#### Waltersburg Deposition

The isolated elongate, slightly curving Waltersburg sand bodies in Illinois (fig. 2) are considered by Potter (1962) to be offshore marine sand bodies deposited parallel to depositional slope. According to his interpretation, these sandstones reflect the most marine conditions under which major sand deposition took place during Chesterian time. On the other hand, Swann's (1964) interpretation of the environment of deposition differs from Potter's in that Swann (1964) considers these Waltersburg deposits to be like the majority of other Chesterian sandstones—deltaic or very near-shore marine in origin. In any case, it can be said with reasonable assurance that the environment of deposition of the major sand bodies found in the Waltersburg Formation ranges from deltaic to shallow-water marine. Therefore, in terms of the classic concepts of oil geology (Hedberg, 1964), the shales of the Waltersburg should have excellent potentials as oil reservoirs.

#### OIL OCCURRENCE

Figure 2 shows the geographic relationships between Waltersburg oil producing trends, sand development, and faulting over a large part of the Illinois Basin. The faults were taken from Swann (1951), Mullins, Lorinsburg, and Hodgson (1965), Ross (1963), and Stonehouse and Wilson (1955). Also shown is the long, unfaulted, apparently continuous sand in Hamilton, Wayne, and White Counties in which no commercial Waltersburg production has been found.

The Roland-Storms-Eldorado producing trend (Trend I) is primarily controlled by sand development. On the other hand, Waltersburg production in the Hovey West-Inman-Junction pools (Trend II) appears to be controlled by structure. In general, the origins of the producing trends shown in figure 2 range between the above two extremes; in addition, local folding is a factor in some areas (Swann, 1951).

Swann (1951) could not find any significant differences in rock types or rock facies between the productive and nonproductive Waltersburg. He also noted that other Chesterian sandstones, notably the Hardinsburg and Palestine, were not productive where their thick sands were developed to the west and south of the Wabash Valley; their oil production was essentially limited to the faulted region in the lower Wabash area. Therefore, he concluded that the oils found in the Waltersburg Formation in the lower Wabash area probably migrated upward along the faults from a deeper source (fig. 2).

Swann and Bell (1958) concluded that the oil production in the Illinois Basin was related to the tops of the three major carbonate sequences. They also found that the distribution of Chesterian production, immediately above the thick Valmeyeran (Middle Mississippian) carbonate sequence, was controlled largely by sand development and structure, and that the absence of Chesterian production in certain areas of the basin could not easily be explained through the use of regional facies maps.

The absence of commercial oil accumulations on the southwest dipping slope, immediately adjacent to the deepest part of the present-day basin, is not restricted to the Waltersburg Formation or even to younger Chesterian rocks. Figure 3 outlines a 40-township area in which virtually no commercial production has been found in any of the Chesterian sandstones and a 55-township area under which there is almost no Cypress production. This Chesterian nonproductive area extends or fingers northward between major oil provinces (Swann and Bell, 1958), which are primarily structural. The area is bounded on the west by the DuQuoin-Louden Anticlinal Belt, and it is interrupted on the south by the large Dale Anticline. Thus, the Chesterian nonproductive area shown on figure 3 is bounded on all four sides by the major structural oil provinces of the basin. However, major commercial oil deposits are found in the subjacent Aux Vases Sandstone throughout the Chesterian nonproductive area.

Sandstones of the Aux Vases are essentially sheetlike in depositional character, and Aux Vases production appears to be in structural rather than stratigraphic traps. Therefore, in the area shown on figure 3, it is likely that many structures are suitable for the entrapment of oil in the Chesterian section. Furthermore, study of Chesterian facies maps (Swann and Bell, 1958; Potter, 1962) shows that the rocks



Figure 3 - Deep basin area in which Chesterian rocks do not produce oil.

in the nonproductive area are essentially the same as the rocks in the surrounding productive regions. Consequently, the absence of Chesterian production in the area shown on figure 3 suggests that a large portion of the Chesterian oils may come from older sediments.

In summary, the evidence, with respect to the origin of Chesterian oils, is contradictory. On the one hand, an indigenous origin is indicated by (1) the environment of deposition of these rocks, and (2) the existence of large volumes of source rocks (shales and limestones) interbedded with high porosity sands capped by shale. On the other hand, a deeper source may be indicated by the absence of Chesterian production in the deep basin area immediately west of the Wabash Valley Fault Complex.

#### EXPERIMENTAL INVESTIGATIONS

#### Analysis of Crude Oil

Twenty-five samples of crude oil were collected for this study. They were obtained at the wellhead from wells completed only in the Waltersburg pay. Each crude sample was collected in a glass container at atmospheric pressure from the bleeder valve of a pumping well. The locations of the wells from which crude oil samples were taken are given in table 1 and are shown in figure 4.

The crude oil samples were shaken with an equal volume of deionized resin water, were centrifuged, and were filtered through dry filter paper. This procedure effectively removed water drops and suspended solids (Nagashima and Machin, 1957). Approximately 3 g of the washed and filtered oil samples were weighed into a Vycor beaker, and the organic matter was destroyed by wet-ashing with 4 ml of 98 percent sulfuric acid at 350 to 400° C. After fuming had ceased, the hot plate temperature was increased to about 500° C. The ashing procedure was similar to that used by Hansen and Hodqkins (1958).

Ash residues were dissolved in 20 percent HCl prepared from constant boiling HCl and deionized water. Nickel and vanadium were quantitatively precipitated from a buffered solution by means of the organic reagent precipitation procedure of Mitchell and Scott (1957), as modified by Shimp et al. (1957). In this method, aluminum and iron were added to the sample solution to serve as carriers for the trace elements during precipitation and to provide a constant matrix of sufficient bulk for spectrographic analysis. The precipitates were dry-ashed at 450° C and were analyzed for nickel and vanadium with the aid of a Bausch and Lomb large prism spectrograph and D,C, are excitation.

This method permitted use of relatively small samples and, consequently, greatly shortened the ashing time. Because of the large concentration factor achieved (approximately 100 times for a 3 g sample and 30 mgs of precipitate), concentrations of nickel and vanadium in the precipitates were far above spectrographic detection limits. Use of larger samples would permit determination of other elements quantitatively precipitated by this method. The coefficients of variation for nickel and vanadium were  $\pm$  9 and  $\pm$ 5 percent, respectively.

Table 1 shows results of spectrographic analyses for nickel and vanadium in the 25 crude oils sampled. In addition, values are given for vanadium to nickel ratios and for API gravities of the crudes.

Fourteen of the samples of Waltersburg crude oil were also analyzed for their light hydrocarbon content by the Esso Research and Engineering Company, Linden,

Sample no.	Location (Sec. T. R., spot)	County	State	Ni (ppm)	V (ppm)	V/Ni	API <sup>1</sup> gravity	Field name
1	13-2S-13W	Gibson	Ind.	4.5	1.2	.26	37.6	Rochester
2	14-3S-12W SE SE NE	Gibson	Ind.	10.3	3.5	.34	29.3	Mounts
3	28-4S-13W NW SW SE	Posey	Ind.	9.5	3.1	.33	36.4	Rogers E
4	9-55-14W E5 NW SE	Posey	Ind.	9.1	3.6	.40	37.0	Griffin C
5	9-5S-14W SE SE SE	Posey	Ind.	11.4	4.6	.40	36.8	Griffin C
6	4-5S-14W NWc SE SW	White	111.	4.6	2.2	.48	36.8	New Harmony C
7	23-58-14W SE SW NW	Posey	Ind.	8.5	3.3	.39	35.8	Springfield C
8	17-6S-12W NW SW SW	Posey	Ind.	14.6	6.0	.41	29.7	Caborn C
9	21-6S-14W NW SE NW	Posey	Ind.	13.3	4.7	.35	33.5	Welborn C
10	36-75-15W NE SW SW	Posey	Ind.	6.5	2.1	.32	37.2	W. Hovey
11	22-85-10E SW SW SW	Gallatin	111.	6.4	2.0	.31	37.2	Inman E C
12	36-85-9E SW SE SW	Gallatin	111.	4.8	1.4	.29	37.2	Junction E
13	16-9S-9E NW SW SW	Gallatin	111.	4.8	2.0	.42	37.4	Junction
14	1-6S-9E SE SW NE	White	111.	6.9	2.6	.38	31.1	Storms C
15	12-65-9E NW SW SE	White	111.	7.0	2.5	.36	32.8	Storms C
16	23-65-9E 70 EL, SW NE	White	111.	9.3	2.6	.28	31.1	Storms C
17	28-6S-9E SE SE SE	White	111.	8.2	2.8	.34	33.0	Herald C
18	33-65-9E SE NW NE	White	111.	9.4	2.9	.31	33.4	Herald C
19	11-75-8E SE NE SE	White	111.	6.2	2.0	.32	31.3	Roland C
20	15 <b>-7</b> 8-8E 581' SL 636' WL NW	White	111.	7.7	2.7	.35	31.1	Roland C
21	21-7S-8E SE SW SW	Gallatin	111.	5.8	2.3	.40	31.0	Roland C
22	29-7S-8E NE NE NW	Gallatin	111.	4.5	1.9	.42	31.0	Roland C
23	15-8S-7E NW NE NE	Saline	111.	1.1	0.3	.30	38.4	Eldorado C
24	33-8S-6E SW NE NE	Saline	111.	0.6	0,2	.33	38.4	Harrisburg
25	15-10S-6E SW NE NE	Saline	111.	0.4	0.2	.50	37.6	Mitchelsville

TABLE 1 - SAMPLE LOCATIONS AND CHEMICAL AND PHYSICAL PROPERTIES OF WALTERSBURG CRUDE OILS

<sup>1</sup>Analyses by W.J. Armon, Associate Chemist, Illinois State Geological Survey.



New Jersey. The locations of the wells from which these samples came are shown on figure 4. For the detailed analysis, each sample was distilled in a 15-plate column at a 5:1 reflux ratio. The IBP-225° F, 225 to 400° F, and 400° F+ bottoms fractions were isolated. The IBP-225° F fractions were analyzed using a gas chromatograph equipped with a silicone column at 75° C and a squaline column at 28° C. This procedure resolves the hydrocarbon components in the C5 through C7 range.

Using samples of the total crude, gas chromatographic analysis resolved the Cg through Cgg normal parafilms, employing a temperature-programmed micro-crystaline wax column with a glass bead support. The internal standard was n-hexadecane. The reported Cg through Cgg parafilm concentrations are probably accurate to  $\pm 10$ percent of the amount actually present. Table 2 summarizes the distillation and chromatographic analyses made for the light hydrocarbons (Cg through Cg and Cg through Cg) in the 14 crude oil samples.

#### Analysis of Shale

The samples of shale were taken from diamond cores on file at the Illinois State Geological Survey. Although over 100 Waltersburg cores are available, only 11 good samples of shale could be found. The locations of the eight wells from which these samples came are shown on figure 4. In general, these samples were hard, well laminated, noncalcareous black shale.

The samples were analyzed using a spectrographic standard addition method. Additions of nickel and vanadium were made to the ground shale, and concentrations in the samples were determined by extrapolation of the calibration curves prepared from the known additions. The results of the shale analyses are given in table 3.

#### DISCUSSION OF RESULTS

#### Trace Elements in Waltersburg Crudes

Figure 5 is a contour map of the nickel concentrations in the Waltersburg crudes of the Illinois Basin. The concentration of nickel varies from 0.4 ppm at the Mitchelsville pool in Saline County, Illinois, to over 14 ppm in the Caborn Consolidated pool in Posey County, Indiana. In general, larger concentrations of nickel and vanadium are found in Indiana than in Illinois. The average nickel concentration in the 8 samples collected in Indiana is 9.1 ppm as opposed to 5.5 ppm in the 16 Illinois samples, These Waltersburg samples have a much greater range of concentrations of the trace metals than the samples of Illinois Basin crudes studied by Witherspoon and Nagashima (1957). Therefore, it is unlikely that trace metal concentrations could be used to segregate Illinois crudes by reservoir age, as was suggested by Witherspoon and Nagashima.

The general decrease in nickel concentration in these crudes to the west and southwest is well shown by the contours in figure 5. Also shown in the figure is a decrease in the nickel concentration to the southwest along the Waltersburg producing trends. As mentioned earlier, producing Trend I is basically controlled by sand development in the Waltersburg Formation, and producing Trend II appears to be controlled by the series of en echelon faults developed in the lower Wabash area. As can be seen in figure 6b and c, some local highs in nickel and vanadium concentrations occur along the Roland-Storms sand body. However, in general, the nickel TABLE 2 - HYDROCARBON CONTENT OF WALTERSBURG CRUDES (VOLUME PERCENT OF CRUDE)

						Walters	burg po	ol name	00					
	Bindsiishurg	Eldorado	W edem0	'N RURMO	pastoa	DUPTON	hleraH	DIRIAN		smrord		916918 Pisleyre	(.bnI111)	Wew Harmony S. (Ind.)
						Sam	ple num	ber <sup>1</sup>						
Hydrocarbon class	24	23	22	21	20	19	18	17	16	15	14	9	4	7
Normal paraffins <sup>2</sup>	14.85	18.64	5.99	6.89	6.82	8.08	5.16	. 66*9	9.56	7.23	7.42	17.53	16.68	17.76
Branched 3 paraffins <sup>3</sup>	1.40	3.83	2.22	1.95	1.34	2.43	3.22	3.90	2.49	1.36	3.07	3.47	3.21	3.00
Naphthenes <sup>4</sup>	1.52	2.87	3.48	2.87	1.86	3.27	3.18	4.24	2.47	2.14	3.45	2.50	2.55	2.68
Aromatics 5	.20	.30	.42	.19	• 06	.15	.04	•00	.42	.25	.14	.23	.40	.33
1 2 2 3 2 9 entane throug 3 7 conentane 2	gh heptan 2 dimet	le, nonan bwlbutan	te throu	igh octa A dimeth	tcosane	(C28).	thylnen	tane.	methy	nentane				1

sopriadate 3. d'auneury souvente, 2, 3 dimetry souvente, 2 metry-pertone, 3 metry-pertones 2.2 dimetry pentane; 2, 4 dimetry pentane; 2 metry lhexane; 2, 3 dimetry ipentane; 3 metry lhexane; 3 ethy pentane.

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content of these crudes decreases to the northeast and to the southeast of the area where this sand body is cut by the fault in southwestern White County. In all of the samples collected, the ratio of the concentration of vanadium to nickel is essentially constant (table 1); therefore, a map of vanadium concentrations shows, for all practical purposes, the same features as figure 5.

The trace metals found in the series of crudes along the faults in Trend II show a slight decrease in concentration to the southwest. However, this decrease is much smaller in magnitude than that found by Silverman (1965) in samples that had apparently migrated less than 3 miles through sandstones. On the other hand, the trace metal contents of the Waltersburg crudes in the Ribeyre Island pool. New Harmony field, shows variations in magnitude similar to those described by Silverman (fig. 6b and c). These crudes apparently have been altered during migration into this pool. However, the high nickel content of some of the Ribeyre Island crudes (>11 ppm) seems to rule out the possibility that these oils migrated for long distances through sandstone of the Waltersburg to reach their present location. Other local variations are found in the trace metal trends shown on figure 5, but in general they do not significantly alter the regional trends. In other words, the trace element contents of these crudes show both persistent regional trends, similar to those described by Silveram (1965).

#### Trace Elements in Shale

Because the Waltersburg crude oils showed a fairly regular decrease in nickel and vanadium content toward the southwest, the nickel and vanadium content of the shales of the Waltersburg were investigated in that area.

In two wells, it was possible to obtain shale samples at different depths. Comparison of these samples shows small and apparently insignificant vertical variations in the concentration of these trace elements (table 3, samples C3 and C5).

As can be seen in figure 7, no regular regional variation occurs in the concentrations of nickel and vanadium in the shales of the Waltersburg. In fact, the variation in trace metal concentrations between samples that are geographically near one another seems to be as large as the variation between samples that are separated by many tens of miles. A slight decrease in the trace metal concentration in the shale appears toward the south and west, but many more samples would be needed to demonstrate that this trend is really significant. Unfortunately, enough core samples are not available to make such a study.

The ratio of vanadium to nickel in the shale samples (table 3) is remarkably constant. In this respect, the trace metal contents of the shales are very similar to trace metal contents of the crude oils (table 1). However, the vanadium concentration is almost twice the nickel concentration in shale, whereas the vanadium concentration is approximately one-third the nickel concentration in the oil.

#### Variation in Waltersburg Crude Gravities

Figure 8 shows the areal variation in the API gravity of Waltersburg olls in the Illinois Basin. Some of the data were obtained in the present study and the remainder collected from the literature (see References—Crude Gravity Data). Reliable information of this kind is difficult to find in the literature, and, therefore, care was taken to evaluate each data source. In some cases, different sources reported widely divergent values of API gravity for crudes that apparently came from the same reservoir. In this event, if a third source could not be found that would verify one of the original sources, the data for that reservoir were discarded. Often gravity data from the same oil pool will differ by 1 or 2° API. This is not surprising, as crude gravities vary during production and vary depending on the position of the sample with respect to the oil-water contact in the reservoir. At any rate, the data used to construct figure 8 should be reliable enough to reveal regional trends in the API gravity of the Waltersburg oils.

The API gravities of Waltersburg crudes generally increase basinward to the south into Kentucky and to the west into Illinois from the area in southwestern Indiana where these crudes have gravities of less than  $30^\circ$  API (fig. 8). A slight increase in crude gravity also appears northeast of this same area, toward the outcrop in Indiana. However, this change is small and may be beyond the reliability limits of the data. In the area around the Roland-Storms sand body, west of the Wabash River in Illinois, crude gravities are surprisingly low for the depth at which the oil is found.

English and Grogan (1948) have discussed the low gravity crudes found in the Hardinsburg and younger Chesterian sands in the Omaha pool (fig. 2), which is immediately to the south of the Roland-Storms producing trend. They concluded that these low gravity oils were related to the igneous intrusives in the Pennsylvanian and Mississippian rocks in this area. They found heavily coked carbonaceous material in some of the oil sands, which indicated that at least some oil had accumulated before the igneous rocks were intruded.

Sample no.	Core no.*	Depth (feet)	Ni (ppm)	V (ppm)	V/Ni†	Remarks
C1	C 1107	2270- 2285	104	174	1.7	Composite sample split from interlaminated siltstone and shale section
C2	C 759	1782	98	238	2.4	
C3	C 3803	153 174 183	61 61 67	91 110 79	1.6 1.8 1.2	Some small brown concretions
C4	C 1244	1493	68	89	1.3	
C5	C 1186	1939 1954	76 67	168 134	2.2 2.0	Some interlaminated silt
C6	C 1978	2270- 2285	82	175	2.1	Composite sample
C7	C 1443	2300	62	83	1.3	
C8	C 359	1895- 1909	78	151	2.0	Composite sample
C9	Outcrop		49	78	1.6	From Potter, Shimp, and Withers (1963)

TABLE 3 - NICKEL AND VANADIUM CONTENT OF SHALES OF THE WALTERSBURG

\*Illinois State Geological Survey. †Average = 1.8. 15

These igneous rocks might provide a convenient explanation for the low gravity Waltersburg crudes in the Roland-Storms area. However, some evidence suggests that the Waltersburg crudes in the Roland-Storms area did not migrate there from the Omaha Dome. Clegg (1955) and Parham (1963) have shown that the igneous dikes or sills in the area of the Omaha Dome were probably intruded at a temperature of from 400 to 600° C and Hodgson and Baker (1957) showed evidence based on laboratory studies that crude oils subjected to temperatures greater than 400° C would rapidly lose, upon subsequent migration, most of their original nickel and vanadium content. Therefore, the trace element concentrations of the Waltersburg crudes in the Roland-Storms sand body seem to be too large to have been the result of such a complex origin. Furthermore, low gravity crudes in the younger Chesterian sands of the lower Wabash area are not uncommon. In fact, the low gravity oils in this area are just too widespread to be related to the Chasi igneous intrusion. It is possible that the low gravity younger Chesterian oils in the lower Wabash area are somehow related to the unlift at the end of Mississionian time.

#### Chemical Variations in Crudes

Table 2 lists the volume percentages of the major classes of hydrocarbons found in the analysis of Waltersburg oils along a line from the Ribeyre Island pool,



Figure 5 - Contour map showing ppm nickel in Waltersburg crudes.



Figure 6 - Schematic diagram of geochemical data from Waltersburg oil pools.





New Harmony field, in White County, Illinois, southwest, through the Roland-Storms and Eldorado pools, to the Harrisburg pool in Saline County, Illinois, Figure 6 is a schematic diagram of these data. The detailed results of the chemical analyses of these crudes is presented in the Appendix, Study of figure 6 shows that the most significant difference between these crudes lies in their content of low molecular weight parafilms ( $\leq C_{20}$ ). The crudes in the Roland-Storms sand body contain much smaller amounts of low molecular weight hydrocarbons than do crudes from the New Harmony, Eldorado, and Harrisburg pools. Variations in the naphthenic and aromatic hydrocarbon content of all these samples seem to be almost random (table 2).

The chemical data for the samples analyzed from the Roland-Storms sand body show that the concentration of the low molecular weight parafins increases to the north away from the area where this sand body is cut by the fault (fig. 6a). However, the two samples collected from the Storms pool, at the extreme northern end of the Roland-Storms sand body, do not fit this trend. In the samples south of the fault, the parafifin concentration, in general, decreases away from the fault. Comparison of the trace metal data and the hydrocarbon data shown in figure 6a, b, and c does not reveal consistent trends, such as Silverman (1965) found. If such trends were present, they might indicate that these crudes had undergone long migrations through the Waltersburg Formation. The chemical variations found in these crudes suggests that local migrations did occur. This is especially true of the three



Figure 8 - Variation in API gravity of Waltersburg crudes.

samples collected from the Ribeyre Island pool. However, along the Roland-Storms trend, the variations in chemical composition between samples from the same oil pool are as large as the variations found between pools. Therefore, it is difficult to separate these samples into small groups that suggest a well defined path of migration away from the fault.

#### SUMMARY

In general, the isocons of the trace quantities of nickel and vanadum found in crudes from the Mississippian Waltersburg Formation in the Illinois Basin are perpendicular to the depositional strike of the basin. The concentrations of these trace metals in these crudes are greatest in Indiana and they decrease progressively basinward to the southwest into Illinois. Some local variations are also found in the trace metal data that suggest that at least some of the Waltersburg crudes have migrated a few miles through the formation. The almost random variations in the naphthene and aromatic contents of the series of crudes from the isolated Waltersburg sand bodies in southeastern Illinois also indicate that these crudes probably accumulated from essentially local sources.

In the Roland-Storms area, where crude movement can be traced away from the fault, the trace metal data, in general, support the fault source hypotheses suggested by Swann (1951). However, if significant quantities of Waltersburg crude did migrate upward from older sediments, one would not expect to find these rather persistent regional trace metal trends in the Waltersburg ols.

In conclusion, the trace metal data show strong regional trends that appear to have been altered locally by short secondary migrations through the Waltersburg Formation. The relation between these trace metal trends and the paleogeography of the ancient basin suggests that trace metals are somehow inherited from the primary source materials from which the crudes were formed.

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APPENDIX

-
Crudes
Waltersburg
of
Compositions
Chemical

				4	olume p	percent	of crud	le – But	anes th	rough (	-			
							Sample	number						
Compound	4	6	7	14	15	16	17	18	19	20	21	22	23	24
Butanes	0.97	1.30	1.35	0.37	0.15	0.32	0.64	0.53	0.20	0.04	0.14	0.24	0.90	0.10
Isopentane	0.75	0.91	0.91	0.58	0.35	0.50	0.84	0.70	0.35	0.16	0.24	0.24	0.90	0.12
n-Pentane	1.15	1.50	1.55	0.25	0.15	0.24	0.37	0.34	0.17	0.07	0.10	0.10	1.74	0.30
2,2 Dimethylbutane	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
2,3 Dimethylbutane	0.04	0.04	0.02	0.05	0.00	0.04	0.06	0.06	0.04	0.03	0.04	0.06	0.05	0.05
2 Methylpentane	0.54	0.67	0.70	0.47	0.28	0.38	0.57	0.52	0.24	0.16	0.20	0.20	0.76	0.30
Cyclopentane	0.20	0.24	0.21	0.25	0.15	0.21	0.27	0.26	0.20	0.12	0.20	0.24	0.23	0.05
3 Methylpentane	0.42	0.50	0.26	0.41	0.24	0.34	0.47	0.44	0.26	0.18	0.24	0.22	0.50	0.19
n-Hexane	1.00	1.16	1.26	0.19	0.12	0.17	0.27	0.25	0.18	0.10	0.11	0.11	1.63	0.78
Methylcyclopentane	0.93	1.00	1.00	1.23	0.66	0.85	1.35	1.24	1.05	0.70	1.11	1.17	0.94	0.32
2.2 Dimethylpentane	0.00	0.01	0.02	0.00	0.00	0.00	0.02	0.03	0.02	0.00	0.03	0.02	0.04	0.01
2,4 Dimethylpentane	0.02	0.00	0.03	0.00	0.00	0.00	0.01	0.03	0.04	0.02	0.04	0.03	0.03	0.02
Cyclohexane	0.37	0.36	0.42	0.61	0.31	0.42	0.68	0.57	0.56	0.36	0.60	0.67	0.52	0.30
2 Methylhexane	0.30	0.28	0.34	0.27	0.13	0.21	0.32	0.25	0.24	0.12	0.20	0.20	0.40	0.23
2, 3 Dimethylpentane	0.08	0.10	0.13	0.15	0.10	0.11	0.19	0.14	0.16	0.10	0.13	0.17	0.15	0.02
3 Methylhexane	0.82	0.75	0.38	0.90	0.17	0.70	1.12	0.77	0.74	0.41	0.60	0.80	0.81	0.37
3 Ethylpentane	0.23	0.21	0.20	0.24	0.09	0.21	0.30	0.28	0.34	0.16	0.23	0.28	0.18	0.09
n-Heptane	0.78	0.72	0.90	0.10	0.05	0.08	0.16	0.10	0.16	0.08	0.07	0.07	1.02	0.80
Benzene	0.10	0.09	0.28	0.02	0.05	0.32	0.03	0.03	0.04	0.03	0.06	0.10	0.15	0.05
Methylcyclohexane	0.58	0.48	0.57	0.77	0.45	0.65	1.12	0.60	1.00	0.40	0.66	0.82	0.75	0.62
Ethylcyclopentane	0.12	0.10	0.10	0.14	0.07	0.09	0.16	0.09	0.14	0.08	0.10	0.13	0.05	0.05
Toluene	0.30	0.14	0.05	0.12	0.20	0.10	0.06	0.01	0.11	0.03	0.13	0.32	0.15	0.15
Other C <sub>7</sub> naphthenes	0.35	0.32	0.38	0.45	0.50	0.25	0.66	0.42	0.32	0.20	0.20	0.45	0.38	0.18

						-								
			Volu	ume pero	cent of	crude -	- c <sub>9</sub> th	cough C	(28) <sup>nor</sup>	mal par	affins			
						S	ample nu	mber						
Compound	4	9	7	14	15	16	17	18	19	20	21	22	23	24
normal Co	06.0	1.20	0.70	0.50	0.60	0.60	0.50	0.40	0.60	0.55	0.50	0.25	0.95	0.95
C,0	1.30	1.40	1.35	0.55	0.60	0.70	0.65	0.30	0.55	0.50	0.45	0.25	0.85	1.50
CTO	1.20	1.10	1.25	0.50	0.60	0.70	0.50	0.30	0.60	0.50	0.55	0.40	1.35	1.30
C11	1.20	1.10	1.20	0.50	0.50	0.65	0.45	0.30	0**0	0.45	0**0	0.35	1.30	1.20
c13 13	1.00	1.00	0.95	0.45	0.45	0.55	0.40	0.25	0.25	0,40	0.40	0.25	1.15	0.85
С, ,	0.90	0.90	0.95	0.45	0.50	0.45	0.40	0.25	0.40	0.35	0.35	0.25	1.10	0.85
C15	0.85	0.80	0.85	0.40	0.50	0.50	0.35	0.25	0.30	0.30	0.30	0.30	0.90	0.75
15	0.80	0.80	0.85	0.40	0.45	0.45	0.28	0.20	0.30	0.30	0.30	0.25	0.90	0.75
CTO	0.75	0.85	0.85	0.35	0.45	0.50	0.20	0.20	0.30	0.35	0.28	0.30	0.80	0.65
C18 18	0.70	0.80	0.80	0.40	0.35	0.70	0.35	0.27	0.45	0.45	0.40	0.25	0.75	0,60
C, S	0.60	0.65	0.65	0.35	0.25	0.60	0.28	0.25	0.45	0.30	0.35	0.40	0.70	0.55
C_5	0.65	0.60	0.65	0.30	0.25	0.45	0.30	0.25	0.45	0.30	0.30	0.28	0.60	0.55
C21	0.55	0.50	0.55	0.30	0.20	0.35	0.25	0.20	0.40	0.30	0.35	0.35	0.55	0.50
C21	0.50	0.50	0.55	0.25	0.20	0.35	0.20	0.20	0.35	0.30	0,40	0.30	0.50	0.45
C <sup>22</sup> 23	0.45	0.45	0.50	0.25	0.20	0.30	0.20	0.20	0.32	0.25	0.25	0.30	0**0	0**0
С.,	0.35	0.40	0.45	0.25	0.20	0.30	0.20	0.17	0.30	0.25	0.25	0.35	0.35	0.30
C 24	0.30	0.35	0.40	0.20	0.18	0.27	0.20	0.15	0.27	0.20	0.20	0.28	0.35	0.25
0.50	0.30	0.30	0.35	0.18	0.18	0.25	0.18	0.13	0.27	0.20	0.20	0.25	0.30	0.20
C21 C21	0.25	0.25	0.35	0.15	0.15	0.20	0.15	0.10	0.25	0.17	0.20	0.20	0.25	0.20
c <sup>21</sup> 28	0.20	0.20	0.25	0.15	0.10	0.20	0.15	0.10	0.18	0.15	0.18	0.15	0.20	0.17

Chemical Compositions of Waltersburg Crudes - Continued

 $\mathbf{^1}_{Analyses}$  by Esso Research and Engineering Company, Linden, New Jersey.

GEOCHEMICAL TRENDS IN WALTERSBURG CRUDES

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### URBANA

# ILLINOIS STATE GEOLOGICAL SURVEY

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