STATE OF ILLINOIS
DEPARTMENT OF REGISTRATION AND EDUCATION

Vanadium in Devonian, Silurian, and Ordovician Crude Oils of Illinois

R. F. Mast
R. R. Ruch
W. F. Meents

ILLINOIS STATE GEOLOGICAL SURVEY
John C. Frye, Chief
Urbana, IL 61801
CIRCULAR 483
1973

VANADIUM IN DEVONIAN, SILURIAN, AND ORDOVICIAN CRUDE OILS OF ILLINOIS

R. F. Mast, R. R. Ruch, and W. F. Meents

ABSTRACT

Fifty-three samples of Devonian, Silurian, and Ordovician crude oil from Illinois were analyzed for their vanadium content by neutron activation analysis. Vanadium concentrations in these samples ranged from 0.03 to 3.72 micrograms per milliliter (μg/ml). Vanadium concentrations were low in crudes that came from reservoirs that were greater than 3200 feet in depth. Maps of vanadium concentrations in these crudes appear to reflect some of the paleostructural features in Illinois, such as the Sparta Shelf and the Sangamon Arch.

INTRODUCTION

Previous studies (Witherspoon and Nagashima, 1957; Mast, Shimp, and Witherspoon, 1968; and Mast, Ruch, and Atherton, 1971) of the trace metal contents of Illinois crudes were directed primarily toward the investigation of nickel and vanadium concentrations in crude oils from Mississippian rocks in Illinois. In general, these studies showed that within individual geologic formations, vanadium and nickel concentrations varied in a regular way over large geographic areas. Vanadium concentrations were found to be abnormally high in areas where early structural deformation could be inferred from isopach maps of the rocks overlying the reservoir rocks. As a result of these studies, it was suggested by Mast, Ruch, and Atherton (1971) that early structural development resulted in the accumulation of some porphyrin-rich materials from petroleum-source beds early in the history of the formation of petroleum or its precursors. This early concentration of these porphyrin-rich constituents influenced the final composition of the crudes investigated.

This investigation was directed toward the study of regional and stratigraphic variations of vanadium content in Devonian, Silurian, and Ordovician crude oils of Illinois. The purpose of the investigation was to determine whether or not maps of the vanadium content of these crudes would reflect some of the early structural features in the Illinois Basin. At present in Illinois there is interest in Silurian reef exploration and in exploration of pre-Mississippian strata in the central basin area. Therefore it was hoped that, by using the concept developed in the studies of Mississippian crudes, studies of pre-Mississippian crudes might give some new information about early structural development in pre-Mississippian strata of Illinois.

SAMPLING PLAN AND CHEMICAL ANALYSIS

Samples of crude oil were collected from Devonian, Silurian, and Ordovician reservoirs. Because the oil production from each of these units is not very widespread in Illinois, all the pools in these units in which singly completed producing wells could be found were sampled. Figure 1 is a generalized geologic column of the pre-Mississippian rocks in Illinois; it shows the units that produce oil in the Devonian, Silurian, and Ordovician strata. The sampling procedures used are the same as those described by Mast, Shimp, and Witherspoon (1968).

About 20 ml of each crude oil sample was washed with ~ 20 ml of deionized water and allowed to settle for a week. The purpose of the wash was to dilute or completely eliminate any possible contamination from the brine accompanying the crude. Various control samples analyzed from the same sources showed the same vanadium contents with and without washing.

An ~ 1.5 ml snap-cap polyethylene vial was filled with the crude, heat-sealed, and promptly irradiated in a thermal neutron flux of 1.4×10^{12} neutrons $cm^{-2} sec^{-1}$ for 30 seconds in the University of Illinois Research Reactor Facility. One (1.0) ml was immediately transferred to an unirradiated vial and counted in a suitable geometry above a 3" x 3" NaI (Tl) detector connected to a 256-channel analyzer. Samples were counted at least twice to confirm the radioactive decay of 3.8 minute ^{52}V. The 1.44 meV gamma-ray photopeak was integrated for quantitative comparison with the photopeak of an aqueous vanadium standard (3.32 μg).

Standards were randomly run throughout an irradiation (1-3 hours) to insure that no significant neutron flux change had occurred. In addition, a control crude oil sample was irradiated and analyzed with each set of samples to check the consistency of values obtained from day to day. The precision of the analytical procedure was estimated to be within ± 15 percent of the measured concentrations.

PRESENTATION OF DATA

The location, field, depth, API gravity, and vanadium concentration of each of the samples are given in table 1. Crude oil gravities were not measured on the samples collected but were taken from previously published data (Armon, Coburn, Mast, and Sherman, 1964; Armon, Lawry, and Mast, 1966) and from some unpublished data available in the records of the Illinois State Geological Survey. Table 1 also lists the location and the oil field name for each of the samples studied.

Vanadium concentrations ranged from 0.03 μg/ml to 3.72 μg/ml (table 1); the average concentrations in 19 Devonian, 21 Silurian, and 13 Ordovician

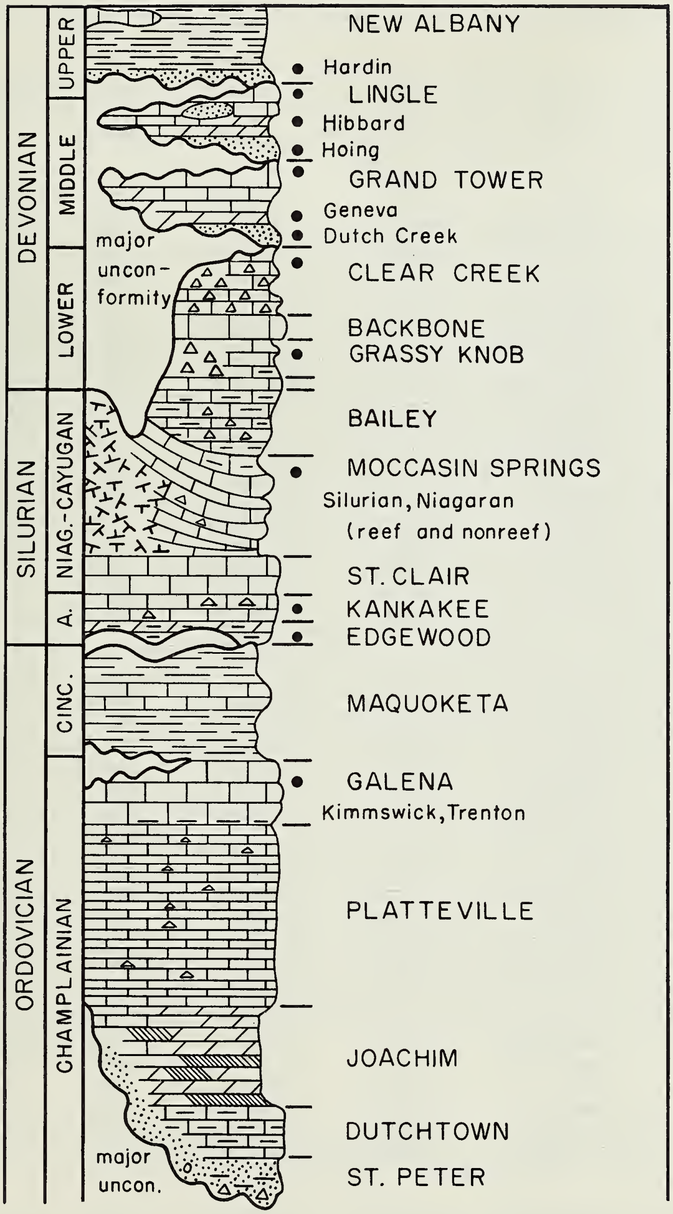


Fig. 1 - Generalized geologic column of Devonian, Silurian, and Ordovician rocks in southern Illinois. Black dots indicate oil and gas pay zones. Formation names are in capital letters only; other pay zones are not. Variable vertical scale. After Van Den Berg and Lawry (1972); originally prepared by David L. Swann.

samples were 0.77, 1.36, and 0.33 μg/ml, respectively. The vanadium concentration found in 109 Mississippian crudes averaged 0.71 μg/ml (Mast, Ruch, and Atherton, 1971).

TABLE 1 - CHEMICAL ANALYSES OF SAMPLES OF CRUDE OIL

System Field	County	Lab. no.	Location Sec.-T.-R.	Depth (ft)	Gravity (^{o}API)	Vanadium (μg/ml)
Devonian						
Aden C.	Wayne	0-1716	16-3S-7E	5320	41.9	0.15
Assumption C.	Christian	0-1727	16-13N-1E	2291	38.4	1.30
Beaucoup	Washington	0-1713	9-2S-2W	3039	38.6	1.62
Boulder E.	Clinton	0-1720	27-3N-1W	2840	34.4	0.43
Centralia	Clinton	0-1719	1-1N-1W	2865	37.4	0.54
Colmar-Plymouth	McDonough	0-1711	19-4N-4W	438	35.2	1.00
Elkton N.	Washington	0-1803	17-2S-4W	2320	--	1.06
Goldengate	Wayne	0-1717	29-2S-9E	5340	39.4	0.24
Irvington	Washington	0-1714	23-1S-1W	3089	38.0	0.19
Kinkaid	Christian	0-1728	3-13N-3W	1793	38.6	1.55
Louden	Fayette	0-1725	8N-3E	3000	28.2	0.61
New Memphis E.	Washington	0-1712	5-1S-4W	2219	40.4	0.84
Posey E.	Clinton	0-1722	15-1N-2W	2737	37.6	0.15
Salem	Marion	0-1721	9-1N-2E	3308	35.2	0.19
Sorento	Bond	0-1723	28-6N-4W	1918	36.8	0.72
Tonti	Marion	0-1802	34-3N-2E	3500	37.0	0.20
Weaver	Clark	0-1726	30-11N-10W	2017	37.0	2.70
Witherton	Fayette	0-1796	13-5N-2E	3466	28.0	0.12
Woburn	Bond	0-1724	3-6N-2W	2270	35.0	0.94
Silurian						
Baldwin	Randolph	0-1731	7-4S-6W	1536	32.1	0.71
Bartelso	Clinton	0-1738	8-1N-3W	2449	41.3	0.85
Bartelso E.	Clinton	0-1736	24-1N-3W	2509	42.0	0.87
Blackland	Macon	0-1742	5-15N-1E	1906	38.6	2.72
Clear Lake E.	Sangamon	0-1744	34-16N-4W	1584	25.4	1.98
Dawson	Sangamon	0-1745	19-16N-3W	1636	--	2.22
Edinburg W.	Christian	0-1797	21-14N-3W	1660	41.0	1.09
Forsyth	Macon	0-1799	24-17N-2E	2118	--	2.34
Frogtown N.	Clinton	0-1739	6-2N-3W	2184	35.2	0.67
Germantown E.	Clinton	0-1737	1-1N-4W	2376	39.4	0.87
Kellerville C.	Adams	0-1730	36-1S-5W	643	36.8	1.19
Marine	Madison	0-1741	9-4N-6W	1733	35.2	0.75
Mt. Auburn	Christian	0-1798	13-15N-2W	1890	37.0	1.79
New Baden E.	Clinton	0-1740	9-1N-5W	1928	39.4	0.78
New Memphis	Clinton	0-1734	3-1S-5W	1932	40.6	1.23
Okawville N.	Washington	0-1735	3-1S-4W	2234	40.0	1.05
Roby E.	Christian	0-1743	24-15N-3W	1840	42.0	1.14
Siloam	Brown	0-1729	9-2S-4W	655	35.0	1.20
Tilden	Randolph	0-1732	16-4S-5W	2143	40.4	0.81
Tilden N.	St. Clair	0-1733	36-3S-6W	2014	42.1	0.58
Wapella	De Witt	0-1746	21-21N-3E	1121	30.6	3.72
Ordovician						
Boyd	Jefferson	0-1750	19-1S-2E	5006	44.9	0.03
Centralia	Clinton	0-1753	35-2N-1W	3976	43.2	0.04
Dupo	St. Clair	0-1800	34-1N-10W	700	33.0	1.12
Hayes	Douglas	0-1759	9-16N-8E	904	30.6	1.23
Irvington	Washington	0-1751	23-1S-1W	4237	38.8	0.16
Patoka	Marion	0-1752	6-3N-1E	3925	41.7	0.03
Posen	Washington	0-1749	21-3S-2W	3878	36.6	0.35
St. Jacob	Madison	0-1755	16-3N-6W	2352	40.0	0.25
St. Jacob	Madison	0-1756	27-3N-6W	2341	40.0	0.45
Salem	Marion	0-1754	6-1N-2E	4492	37.0	0.04
Turkey Bend	Perry	0-1748	10-4S-2W	3937	35.4	0.33
Westfield	Clark	0-1758	5-11N-14W	2390	38.2	0.08
Woburn	Bond	0-1757	21-6N-2W	3151	38.6	0.15

RESERVOIR DEPTH, OIL GRAVITY, AND VANADIUM CONCENTRATION IN CRUDES

Mast, Ruch, and Atherton (1971) found no relationships between reservoir depth and vanadium concentration nor between oil gravity and vanadium concentration in Mississippian crudes. Figures 2 and 3 show crossplots of these same parameters for the Devonian, Silurian, and Ordovician and for all the samples analyzed in this study.

Vanadium concentrations decrease somewhat with depth in Devonian and Ordovician crudes but not in Silurian crudes (see fig. 2). In crude samples from depths greater than 3200 feet, no vanadium concentrations greater than 0.4 μg/ml were found. The fact that none of the Silurian samples exceeded 2600 feet in depth may explain in part why no concentration-depth relationships were found in Silurian crudes. Although more samples are needed to reach a firm conclusion, the data presented in figure 2 suggest that thermal maturation influences vanadium contents in crudes below a certain threshold depth.

This same threshold depth hypothesis might also be used to explain the absence of any depth-vanadium relationships in previously published data for samples of Mississippian crudes from Illinois (Mast, Ruch, and Atherton, 1971). Almost all of those samples came from reservoirs less than 3200 feet in depth. It has been suggested by Damberger (1971) from studies of coal rank in Illinois that erosion may have removed more than a mile of post-Mississippian rocks from Illinois. If erosion was that extensive, a present depth of 3200 feet for these crudes could correspond to a depth of burial in excess of 8500 feet in the geologic past. The threshold depth hypothesis suggested by the vanadium data in this study is similar to that suggested by Vredenburgh and Cheney (1971). They found that nonbiological thermal desulfurization of Wyoming Paleozoic crudes occurs below a threshold depth that exceeds 9000 feet.

Figure 3 shows crossplots of vanadium concentration and crude oil gravity. Although there appears to be a relation between these two parameters in the Ordovician samples studied, no relation shows for the Devonian and Silurian crudes. No relation was found between these two parameters by Mast, Ruch, and Atherton (1971) in Mississippian crudes from Illinois. On the other hand, Hodgson (1954), working with Cretaceous to Devonian crudes, found relationships between depth and vanadium concentration and between gravity and vanadium concentration.

DISTRIBUTIONS OF VANADIUM CONCENTRATION IN DEVONIAN, SILURIAN, AND ORDOVICIAN CRUDES

Figure 4 shows the distribution of vanadium concentrations in crudes from each of the three systems sampled and the distribution for all of the samples used in this study. In general, these distributions are all skewed to the right and cover approximately the same concentration ranges.

There generally appears to be no significant difference in the vanadium concentrations in crudes from Mississippian, Devonian, Silurian, and Ordovician rocks that might be attributed to possible variations in source material. A possible exception to this is found in the Ordovician crudes (see fig. 4), in which the mean concentration and the concentration range are somewhat smaller than those found in the other oils studied. However, the samples of Ordovician

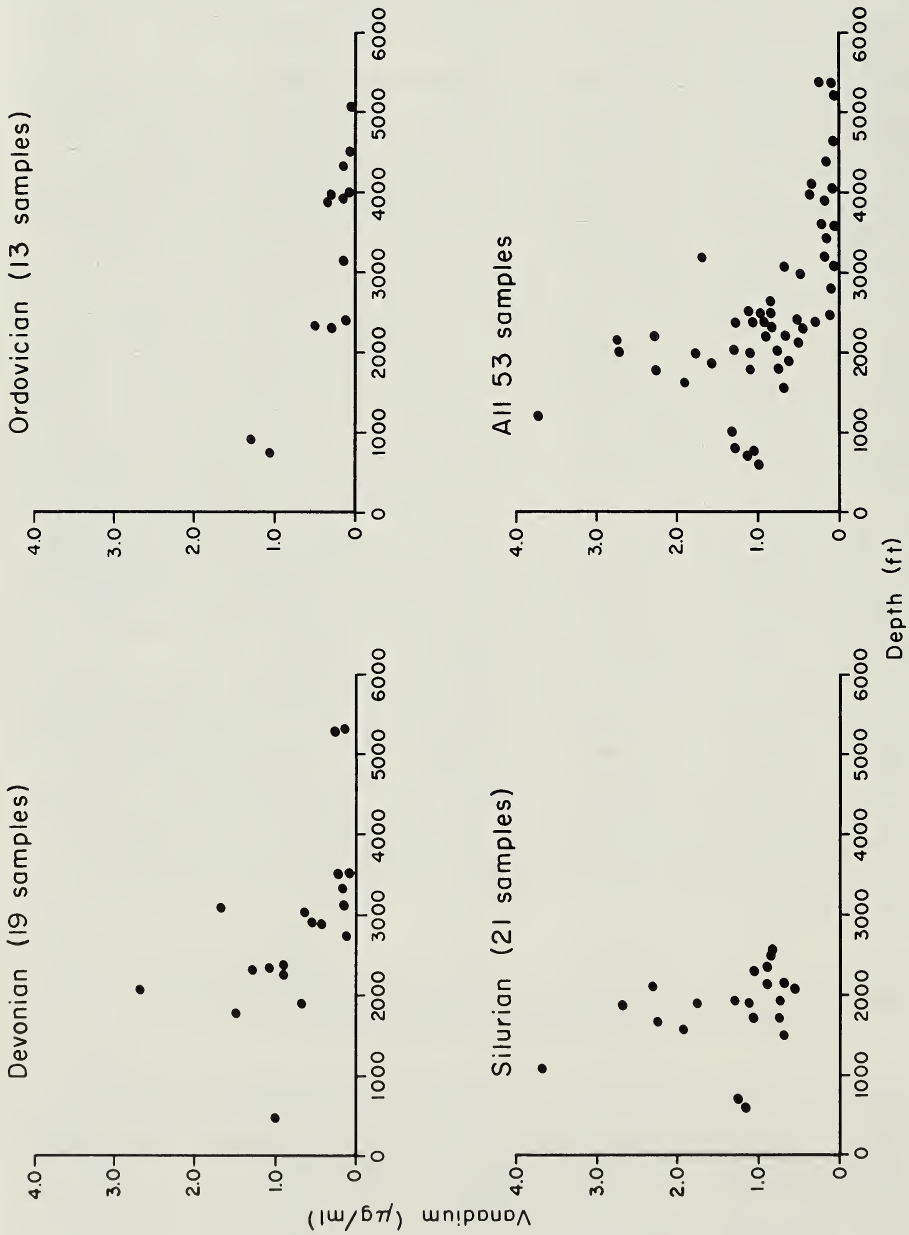


Fig. 2 - Crossplots of reservoir depth and vanadium content.

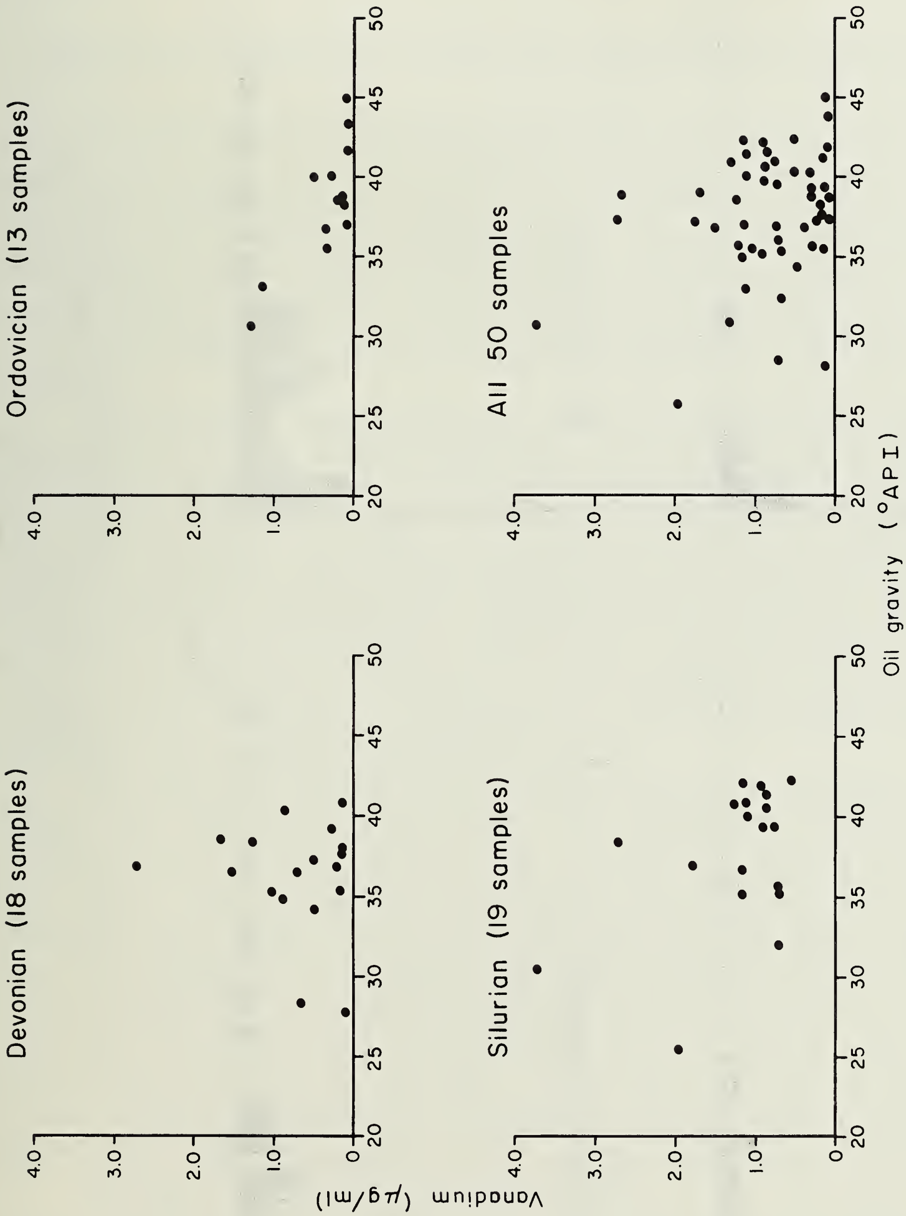


Fig. 3 - Crossplots of crude oil gravity and vanadium content.

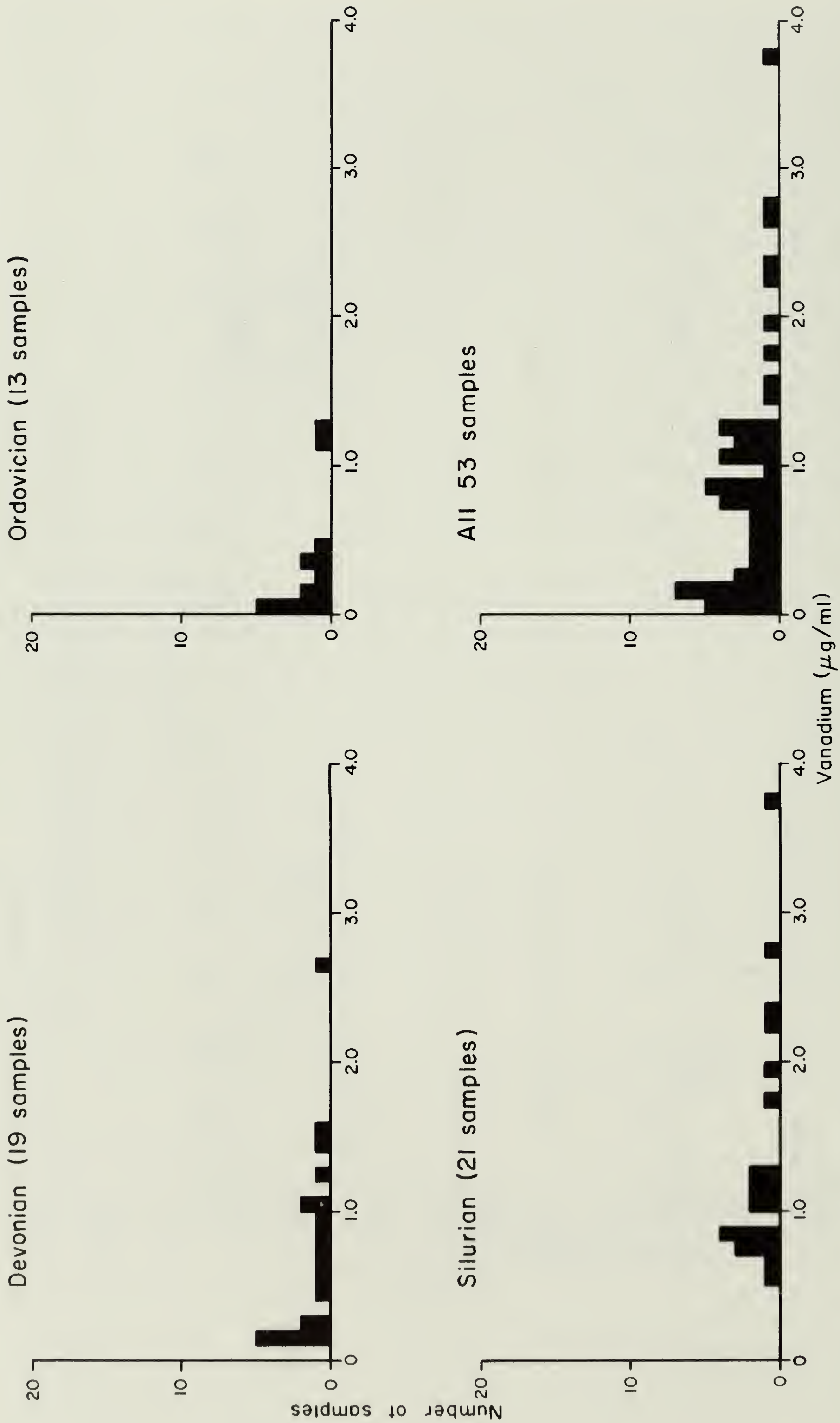


Fig. 4 - Distribution of vanadium in Devonian, Silurian, and Ordovician crudes.

crudes generally came from deeper reservoirs than did the Devonian and Silurian samples. The low concentrations of vanadium in Ordovician samples are probably the result of maturation and therefore not related to variations in source material.

GEOGRAPHIC VARIATIONS IN VANADIUM CONCENTRATIONS IN CRUDES

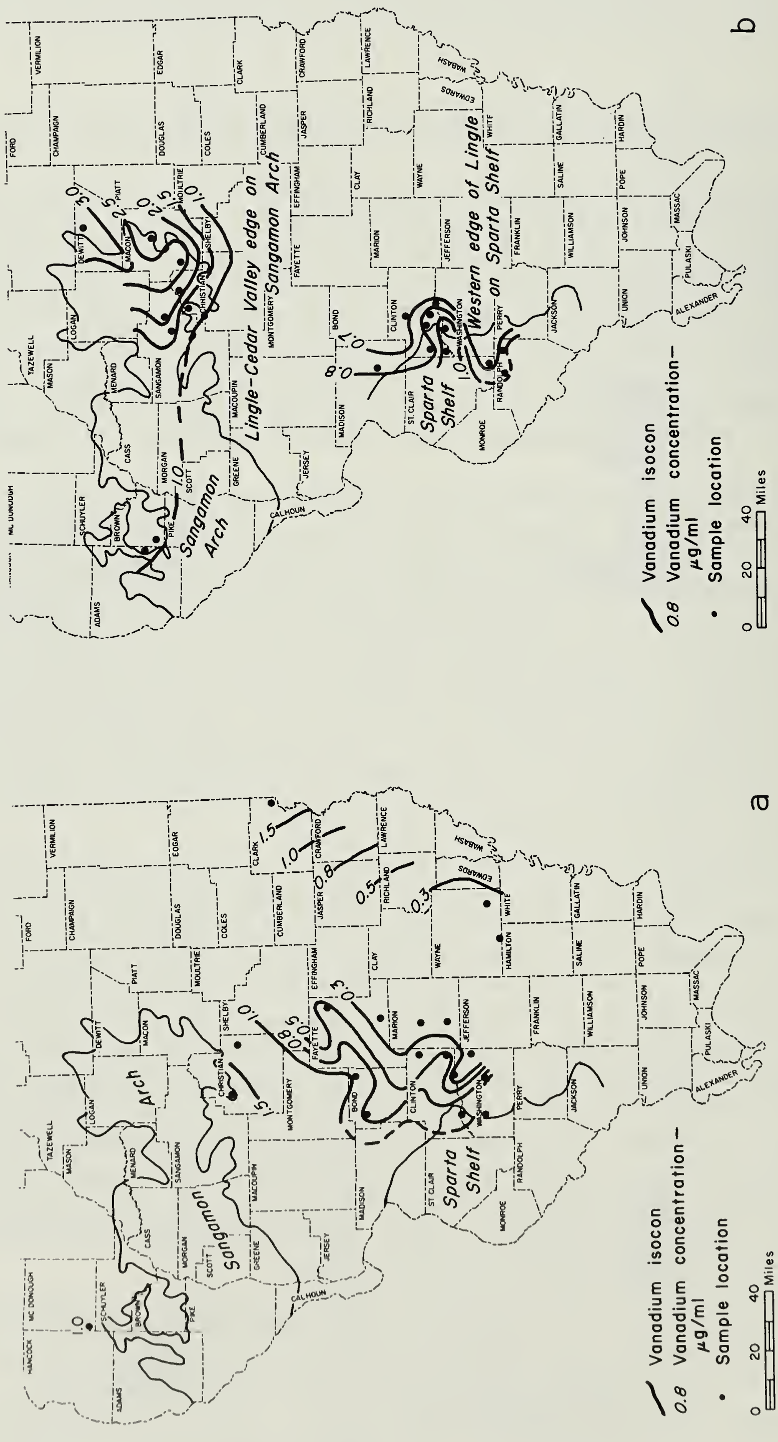
The vanadium concentrations given in table 1 are plotted and contoured in figures 5a, b, and c for the Devonian, Silurian, and Ordovician oils. In general, the isocons on these maps follow the structural configuration of the basin. High concentrations of vanadium are usually found close to the margins of the basin, and vanadium concentration in the crudes decreases basinward. These patterns are very similar to those found in Cypress, Aux Vases, and Ste. Genevieve crudes (Mast, Ruch, and Atherton, 1971) in Illinois. There are, however, significant differences in the contour map patterns shown on figures 5a, b, and c, and these differences appear to reflect some of the paleostructures in Illinois.

High vanadium concentrations are found in the Devonian oils (fig. 5a) in Washington and Clinton Counties in the area of the Sparta Shelf (Meents and Swann, 1965). High vanadium concentrations were also found in northern Bond County on the flanks of the Sparta Shelf and in Christian County on what was during Middle Devonian time the southern flank of the Sangamon Arch (Whiting and Stevenson, 1965). The vanadium highs in these two areas correspond reasonably well to local thinning of the overlying Grassy Creek-New Albany shales as mapped by Workman and Gillette (1956, fig. 6). Their map also shows thinning to the northeast from northern Bond County through Fayette County along a Devonian structural feature that they named the Vandalia Arch. On this arch in northeastern Fayette County, a sample of Devonian crude from the Louden field had a fairly high vanadium content — 0.61 μg/ml.

The geographic distribution of vanadium in Silurian crudes (fig. 5b) is similar to that found in Devonian crudes. Also shown on figure 5b are the zero thickness contours of the correlative Lingle and Cedar Valley Limestones on the flanks of the Sangamon Arch and the Lingle Limestone on the flanks of the Sparta Shelf. These contours were taken from Whiting and Stevenson (1965) and from Meents and Swann (1965). The overlapping of the subjacent Grand Tower Limestone by the Lingle and Cedar Valley Limestones shows that both the Sparta Shelf and the Sangamon Arch were positive features during Middle Devonian time. Figures 5a and b show that there is a relationship between vanadium concentrations in Devonian and Silurian crudes and the paleogeographic features that developed during Middle and Upper Devonian time. This relationship supports the hypothesis that vanadium concentrations in crudes are related to early structural development (Mast, Ruch, and Atherton, 1971). In deep Devonian and Ordovician crudes they may also be related to depth of burial.

From maps of reef oil pools in southwestern Illinois it is difficult to determine whether there is one reef trend to the north-northeast or two reef trends to the northeast (see fig. 6). From the vanadium contours of the Silurian reef crudes in figure 5b, it appears that there are two northeast reef trends.

Vanadium concentration of crudes may be a valid criterion for associating reefs into trends. Stevenson (1973) has suggested that Galena (Trenton) structure


a
Sangamon Arch
Sparta Shelf
Vanadium isocon
0.8 Vanadium concentration—μg/ml
Sample location
0 20 40 Miles
b
Lingle-Cedar Valley edge on Sangamon Arch
Sangamon Arch
Western edge of Lingle on Sparta Shelf
Sparta Shelf
Vanadium isocon
0.8 Vanadium concentration—μg/ml
Sample location
0 20 40 Miles

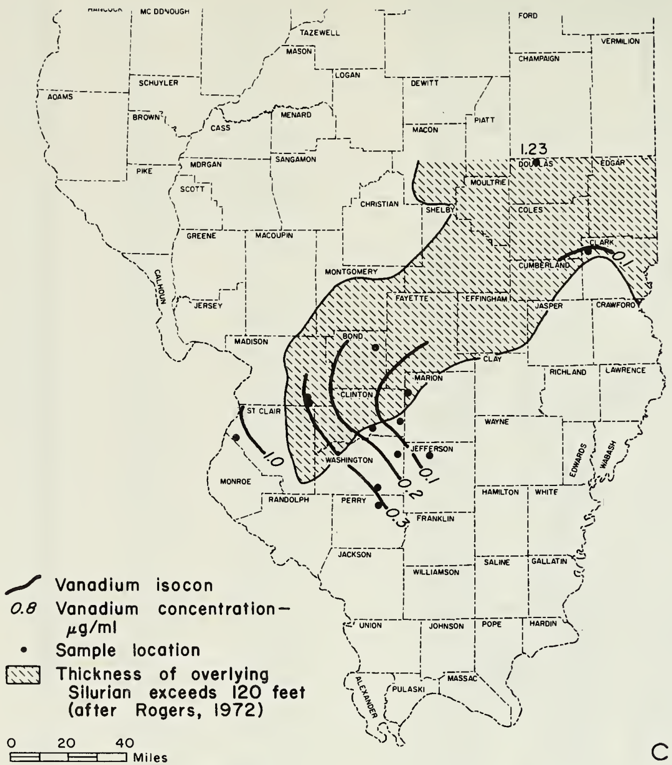


Fig. 5a - Vanadium in Devonian crudes.
b - Vanadium in Silurian crudes.
c - Vanadium in Ordovician crudes.

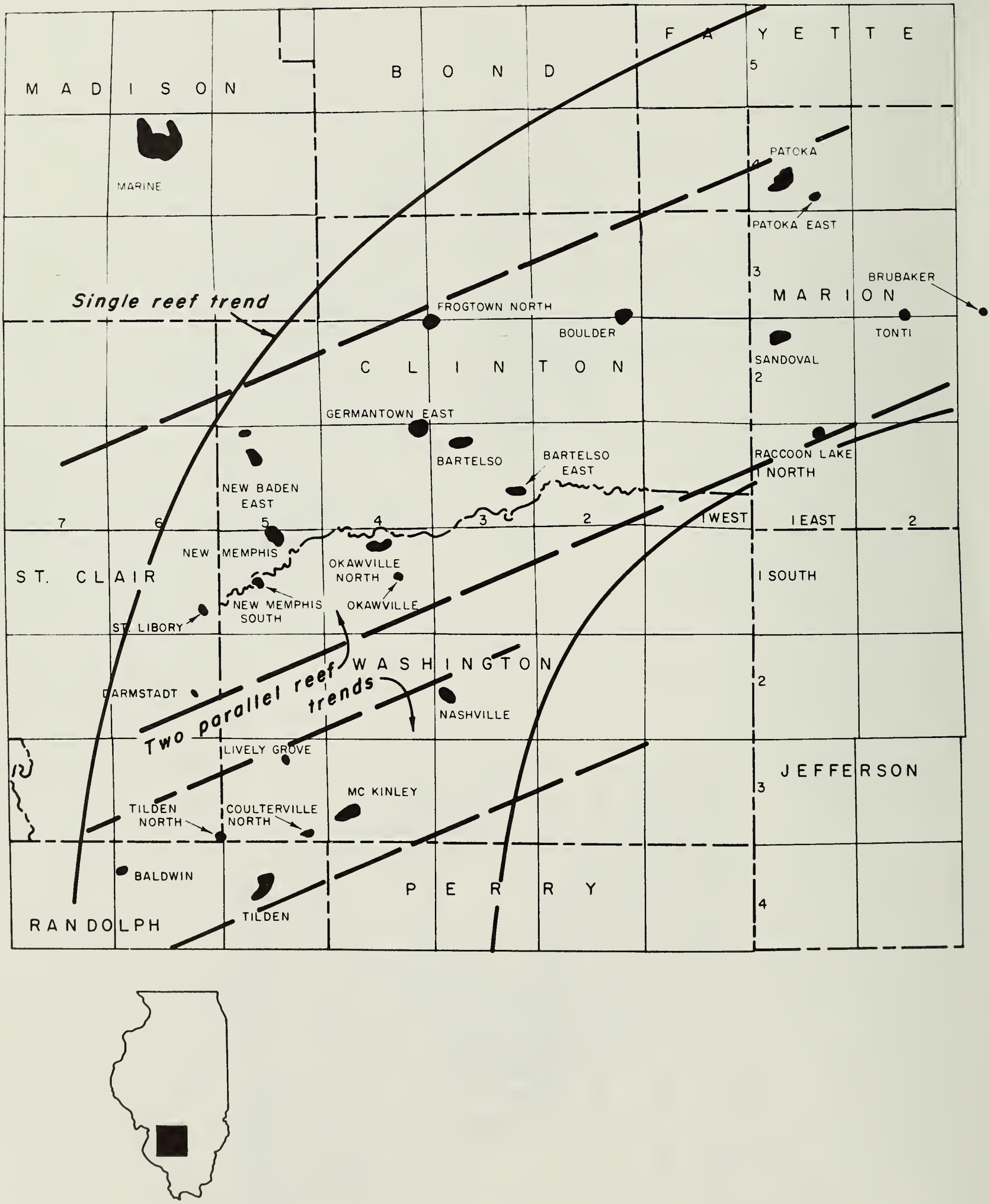


Fig. 6 - Two alternative interpretations of reef trends in southwestern Illinois.

influenced reef growth on the Silurian sea floor and that some thickness variations in beds overlying the reefs may be due to a post-Silurian uplift of these same structures. If these structures parallel the reef trends, the post-Silurian uplift would have caused oil to migrate into the reefs along each trend. If each reef trend was in fact a separate center for oil accumulation, that might explain the variations in vanadium concentrations which appear to separate these trends (fig. 5b).

On figure 5c, vanadium concentrations in Ordovician (Trenton) crudes in Illinois are contoured. The contours on this figure follow reasonably well the thickness contours for the Silurian rocks in western Illinois, as shown by Rogers (1972, fig. 4).

It is interesting to compare figure 5b with 5c in western Illinois. In figure 5b, vanadium contours are convex to the east as are the overlying Middle and Upper Devonian thickness contours on the Sparta Shelf. Conversely, in figure 5c, vanadium contours are convex to the west, as are the overlying Silurian thickness contours in the same area. Although contours of vanadium concentration in Ordovician crudes may be related to the thickness of the overlying Silurian rocks, vanadium concentration in these crudes may have been altered by depth of burial.

SUMMARY

Vanadium concentrations in Devonian, Silurian, and Ordovician crudes are similar to those found in Mississippian crudes (Mast, Ruch, and Atherton, 1971) in Illinois. Devonian, Silurian, and Ordovician crudes contain an average of 0.89 μg/ml of vanadium. In general, vanadium concentrations in pre-Mississippian crudes decrease basinward and decrease with increasing depth. The data suggest that maturation becomes important below a paleoburial depth of 8500 feet.

Comparison of the geographic distributions of vanadium in Devonian and Silurian crudes shows that vanadium concentrations are high around areas like the Sparta Shelf and the Sangamon Arch that were structurally high during Middle and Upper Devonian time.

Contours of vanadium concentrations in Silurian reef crudes in southwestern Illinois appear to separate these reef pools into two producing trends.

REFERENCES

Armon, W. J., A. A. Coburn, R. F. Mast, and C. W. Sherman, 1964, Physical properties of Illinois crude oil — Part I: Illinois Geol. Survey Illinois Petroleum 78, 53 p.

Armon, W. J., T. F. Lawry, and R. F. Mast, 1966, Physical properties of Illinois crude oil — Part II: Illinois Geol. Survey Illinois Petroleum 81, 44 p.

Damberger, H. H., 1971, Coalification pattern of the Illinois Basin: Jour. Econ. Geol., v. 66, p. 488-494.

Hodgson, G. W., 1954, Vanadium, nickel and iron trace metals in crude oils of western Canada: Am. Assoc. Petroleum Geologists Bull., v. 38, p. 2537-2554.

Mast, R. F., R. R. Ruch, and Elwood Atherton, 1971, Vanadium in Cypress, Aux Vases, and Ste. Genevieve crude oils of Illinois, in Bond, D. C., chairman, Proceedings of symposium on future petroleum potential of NPC Region 9 (Illinois Basin, Cincinnati Arch, and northern part of Mississippi Embayment): Illinois Geol. Survey Illinois Petroleum 95, p. 111-126.

Mast, R. F., N. F. Shimp, and P. A. Witherspoon, Jr., 1968, Geochemical trends in Chesterian (Upper Mississippian) Waltersburg crude of the Illinois Basin: Illinois Geol. Survey Circ. 421, 23 p.

Meents, W. F., and D. H. Swann, 1965, Grand Tower Limestone (Devonian) of southern Illinois: Illinois Geol. Survey Circ. 389, 34 p.

Rogers, J. E., 1972, Silurian and Lower Devonian stratigraphy and paleo-basin development: Illinois Basin — central United States: Unpublished Ph.D. thesis, University of Illinois, Dept. of Geology, Urbana, Illinois.

Stevenson, D. L., 1973, The effect of buried Niagaran reefs on overlying sediments: Illinois Geol. Survey Circ. 482, 22 p.

Van Den Berg, Jacob, and T. F. Lawry, 1972, Petroleum industry in Illinois, 1971: Illinois Geol. Survey Illinois Petroleum 98, 120 p.

Vredenburgh, L. D., and E. S. Cheney, 1971, Sulfur and carbon isotopic investigation of petroleum, Wind River Basin, Wyoming: Am. Assoc. Petroleum Geologists Bull., v. 55, no. 11, p. 1954-1975.

Whiting, L. L., and D. L. Stevenson, 1965, The Sangamon Arch: Illinois Geol. Survey Circ. 383, 20 p.

Witherspoon, P. A., Jr., and Kozo Nagashima, 1957, Use of trace metals to identify Illinois crude oils: Illinois Geol. Survey Circ. 239, 16 p.

Workman, L. E., and Tracey Gillette, 1956, Subsurface stratigraphy of the Kinderhook Series in Illinois: Illinois Geol. Survey Rept. Inv. 189, 46 p.

Illinois State Geological Survey Circular 483
14 p., 6 figs., 1 table, 2000 cop., 1973
Urbana, Illinois 61801

Printed by Authority of State of Illinois, Ch. 127, IRS, Par. 58.25.

CIRCULAR 483

ILLINOIS STATE GEOLOGICAL SURVEY

URBANA, IL 61801