



STATE OF ILLINOIS

DEPARTMENT OF REGISTRATION AND EDUCATION

PREDICTION OF SILURIAN REEF LOCATIONS THROUGH TRACE ELEMENT PROFILES

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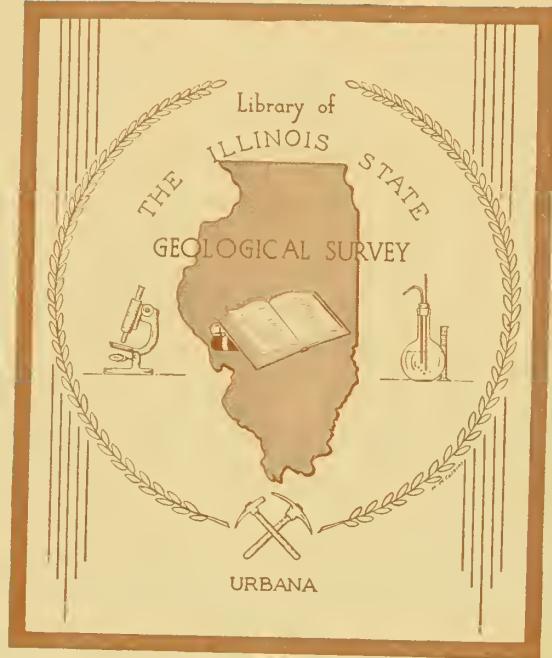
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ILLINOIS PETROLEUM 113

ILLINOIS STATE GEOLOGICAL SURVEY
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Prediction of Silurian Reef Locations through Trace Element Profiles

R. A. Cahill, J. A. Schleicher, W. F. Meents,
Chao-Li Liu, and R. R. Ruch

ABSTRACT

This investigation studies the use of certain trace element concentrations as geochemical indicators to distinguish between reef and nonreef material in southern Illinois carbonates. In addition, geochemical criteria were used to predict the distance of a sample from a reef. Thirty-two elements were determined on 63 Silurian rock samples grouped according to their locations. With the use of a discriminant analysis function, 50 of the 63 samples were correctly classified. This method has potential for predicting the locations of unknown reefs and possible petroleum accumulations.

INTRODUCTION

In today's energy demanding world, the need to increase known petroleum reserves is critical. Former areas of production must now be reinvestigated for untapped small deposits or for application of secondary and tertiary recovery techniques. In many parts of the world organic reefs and reef facies have proven to be associated with highly productive petroleum reservoirs. In the Great Lakes area and in Illinois in particular, Silurian reefs have been sought for 30 years, since Lowenstam and Dubois (1946) found that the oil-producing horizon in the Marine field was a Silurian reef structure. For the thick Silurian section of southwestern Indiana, future exploration is advocated by Becker and Keller (1976).

But the problem of locating and defining ancient reefs in the subsurface is complex and requires extensive investigation. The American Association of Petroleum Geologists in a reprint series (1975) noted that over 75 major papers had addressed the subject in its bulletin alone. The difficulty

in locating ancient reefs led Shaver (1974) to note in his study area of northern Indiana that perhaps thousands of reefs are yet undiscovered or were destroyed by Devonian erosion. In an extensive literature survey of both recent and ancient reefs, Braithwaite (1973) defined "reef" and suggested the following criteria for recognition of reefs: (1) relief, (2) environmental variation, (3) zonation, (4) nature of organisms, and (5) internal structure.

Geochemical data can be used to supplement lithologic and paleontologic methods in establishing sediment facies. Trace element analysis and relations between elements can indicate past Eh, pH, and the depositional environment. Variations in trace elements may be due to sorption, presence of organic matter, diagensis, biological activity, and leaching. With the advent of more accurate and multi-elemental analytical techniques, the geochemist is often provided with a large amount of chemical data for problem solving. Considerable work has been done on the nature of trace element association in coal and petroleum to elucidate past geological environments and the source of mineral deposits; for example: Gluskoter et al. (1977), Swanson et al. (1976), Bonham (1956), Bailey et al. (1974), and Hitchon et al. (1974).

The application of trace element data to the study of carbonates in general and reef structures in particular has been investigated by various workers. Trace element concentrations in carbonate rocks have been summarized by Graf (1960) as well as (Krauskopf, (1955); Keith and Degens, (1959); Chester, (1965); Kitano et al., (1973); Klemm, (1973); Al-Shahristani et al., (1973); and Barber, (1974)). Using published data, Graf (1960) separated elements associated with carbonate rocks into four groups: (1) those

being absorbed on surfaces, (2) those incorporated into a solid solution with the carbonate minerals and accessory authigenic precipitates, (3) noncarbonate skeletal material, and (4) organic matter altered during diagenesis. Kitano et al. (1973) measured the difference in distribution coefficient values for Zn, Cu, Mg, Sr, Ba, and U between carbonate precipitates and solutions. Among the controlling factors that he found for trace element concentration in marine calcareous skeletons were the crystal form of the calcite precipitate, type and concentration of organic matter, temperature, salinity, and trace element concentration in the initial solution. The organic material in carbonate rocks has often been suspected of being the source of enrichment for many trace elements.

The use of trace element concentrations as indicators of the environment of deposition of sediments was investigated by Keith and Degens (1959), in an attempt to distinguish marine from nonmarine shales. The variation in the trace element content of a series of carbonate rocks of Devonian age was studied by Chester (1965), who found that Co, V, Cr, Ni, and Ba concentrations and ratios could be used as indicators in distinguishing reef from nonreef carbonate materials.

Chester (1965) also suggested that the distribution of trace elements in the total sample as well as in the acid-soluble (nondetrital) fraction should be analyzed, since the detrital source material would be influenced by the physical variables in the area which may have been perturbed by the presence of reef structures, which would affect current and depositional patterns. He also pointed out that if significant variability in a trace element concentration across a basin of deposition can be related to the type of environment in the area, then that element may be a useful geochemical indicator.

Our study is an investigation of the feasibility of using trace element concentrations as geochemical indicators to distinguish between reef and nonreef material in southern Illinois Silurian carbonates. In addition, we explored the feasibility of using geochemical parameters to predict the distance from a sample to a reef, a more difficult problem but of greater significance in exploring for new reef structures.

The elements determined in the study were: by X-ray fluorescence—aluminum, calcium, iron, phosphorus, silicon, titanium,

vanadium, magnesium, and sulfur; by instrumental neutron activation—bromine, potassium, sodium, arsenic, gallium, manganese, scandium, samarium, europium, lanthanum, and antimony; and by radiochemical separation—mercury. Most of the data obtained by optical emission spectroscopy were below the method limit of detectability. Further refinement of the technique for the analysis of carbonate material is one area which can be explored to include a number of potentially useful elements.

GENERAL GEOLOGY OF THE AREA

In the counties of Clinton, Madison, Marion, Randolph, St. Clair, and Washington in Southwestern Illinois (fig. 1), petroleum-bearing reefs have been found in rocks of the Silurian System (fig. 2). The Silurian stratigraphy is described in detail by Willman (1975). Reef growth started in the Illinois Basin during deposition of the St. Clair Limestone. The large reefs studied in this report are in the Moccasin Springs Formation and commonly are roughly circular, (figs. 3 to 8) with diameters ranging up to about 3.5 miles (5.6 km) and vertical dimensions ranging up to nearly 1000 feet (300 m). More than one center of growth may result in a complex (figs. 9 to 11), so that the large Marine reef, for example, is rather like a horseshoe.

The Moccasin Springs reefs of this report, consisting of relatively pure carbonate rock, are surrounded by an interreef facies of impure carbonates and calcareous siltstones. Lowenstam (1949) describes their composition:

"The reef-rock proper always consists of practically pure carbonates, either limestone or dolomite, that have higher electrical resistivity than normal interreef rocks. Reef dolomites are invariably blue-gray in color, coarse-grained, and vesicular. Reef limestones are pink to white coquinas, formed almost exclusively of coarse unsorted fossil debris in which corals and stromatoporoids are important constituents. Chert is never present."

The interreef facies is variable but consists predominantly of red and greenish-gray, very fine-grained silty, argillaceous carbonate and calcareous argillaceous siltstone. In the south the carbonate is mainly red limestone. To the north the red portion thins,

and more and more of the upper part of the facies is greenish-gray, very cherty dolomite.

Some of the interreef samples are from the Lower Devonian Bailey Limestone (fig. 12) a thick, gray to greenish-gray, silty, cherty, very hard limestone. The tops of the reefs stood above the sea bottom in Early Devonian time, so that some reef wash may have been included in the Bailey. There is even a possibility that reef growth may have persisted from the Silurian into Early Devonian time. The fossils in the Bailey are sparse, but a few found in the lower part of the formation indicate a Silurian age. The entire Bailey has been assigned to the Devonian because no obvious lithologic indication of a difference between the Silurian and Devonian portions is known.

The reef-rocks are characterized by their high purity, being, as a rule, 98 percent or more carbonates. The only common insoluble material is secondary pyrite. In contrast, the interreef rocks in the region of the reef archipelago average about 40 percent insoluble. The reef cores are flanked by beds of reef-derived detritus which dip radially away from the core. Reef-wash, beds of well sorted fossil debris, may extend some distance from a reef, fingering out into the impure interreef strata.

SAMPLE DESCRIPTION AND EXPERIMENTAL PROCEDURES

All the samples analyzed were taken from drill cores submitted to the Illinois State Geological Survey by petroleum companies. The descriptions of the 63 Silurian rock samples analyzed are given in table 1. Table 2 lists the locations and depth intervals of 19 individual samples taken from 5 cores, which were analyzed to study the vertical variation of trace elements within an individual core. Figure 13 is an index map of the samples studied.

Chemical analyses were performed on core samples which had been ground to less than 100 mesh. The precision and accuracy vary for each element and also according to the method employed. For instrumental neutron activation the results for sodium, potassium, gallium, lanthanum, manganese, samarium, and europium are 10 percent or less relative error, while for bromine, arsenic, antimony, and scandium the relative error is higher (15 to 30 percent) largely due to poorer

counting statistics. The errors involved in X-ray fluorescence are due primarily to matrix effects but are less than ± 10 percent relative concentrations for most elements. Details of the two methods of analyses are found elsewhere (Gluskoter et al., 1977). Of particular note here is that absolute accuracy is not critical since the establishment of relative differences between samples is the primary interest. Any particular bias a method or element has (unless severe) would not adversely affect the final outcome of the stated objectives of the study.

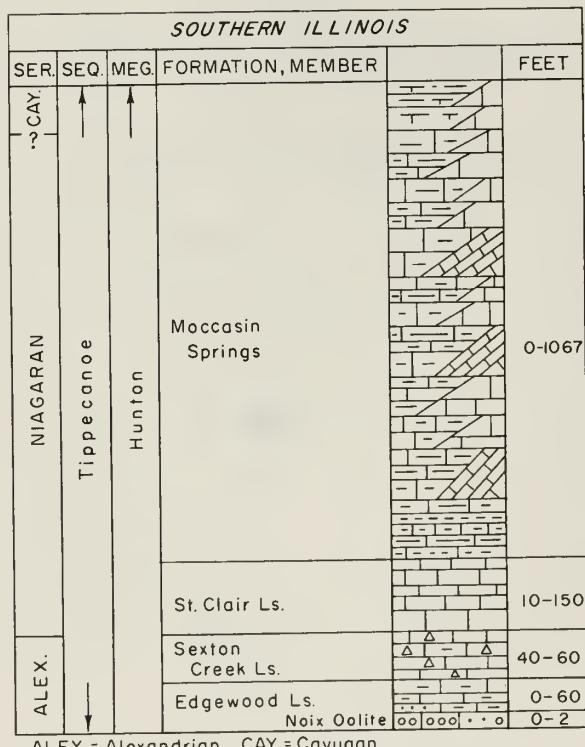


Fig. 1 - Columnar section of the Silurian System in southern Illinois.

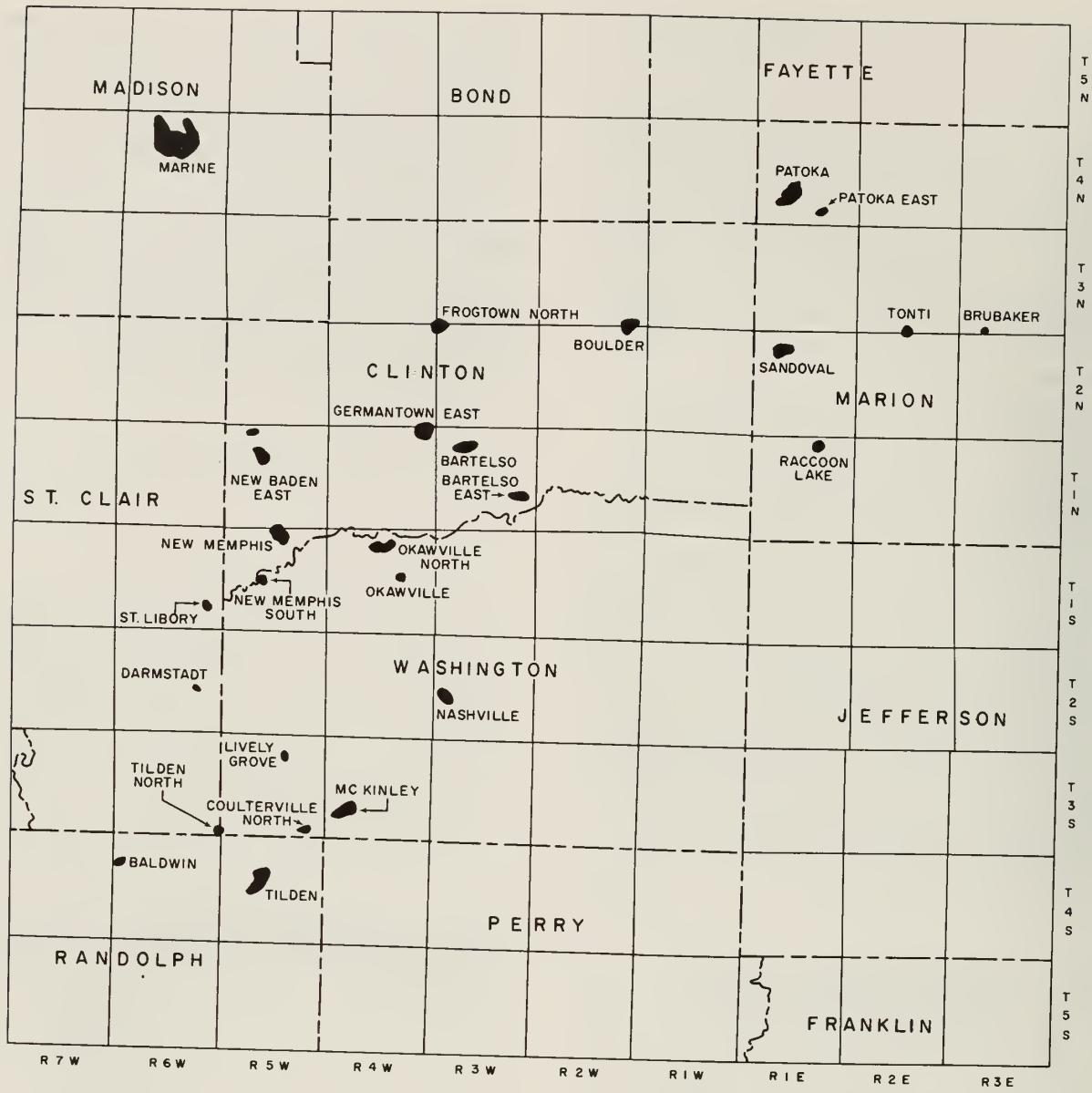


Fig. 2 - Silurian reefs, Southwestern Illinois, July 1973.

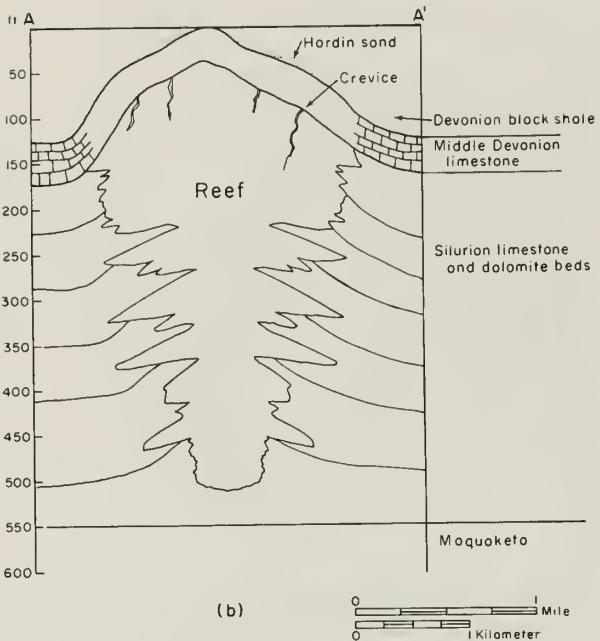
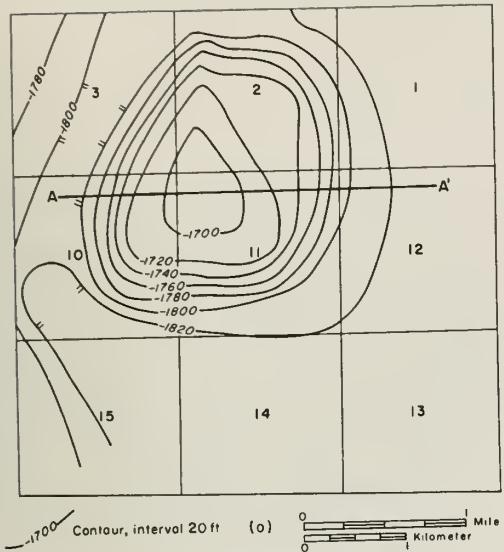


Fig. 3 - Structure map (A) of a typical pinnacle reef contoured on the top of the Hunton Megagroup and a cross section (B) of the reef (vertical \times 25).

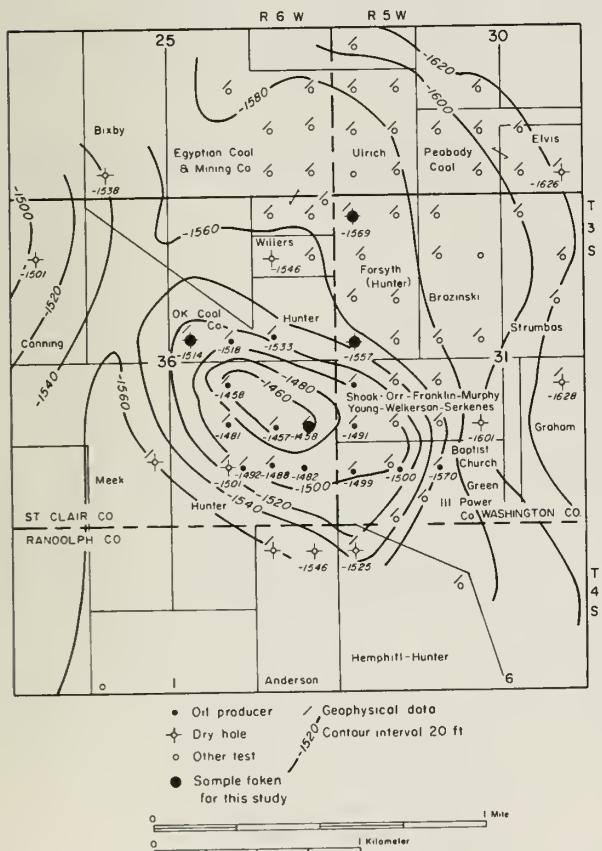


Fig. 4 - Structure map of the Tilden North field drawn on top of the Silurian reef.

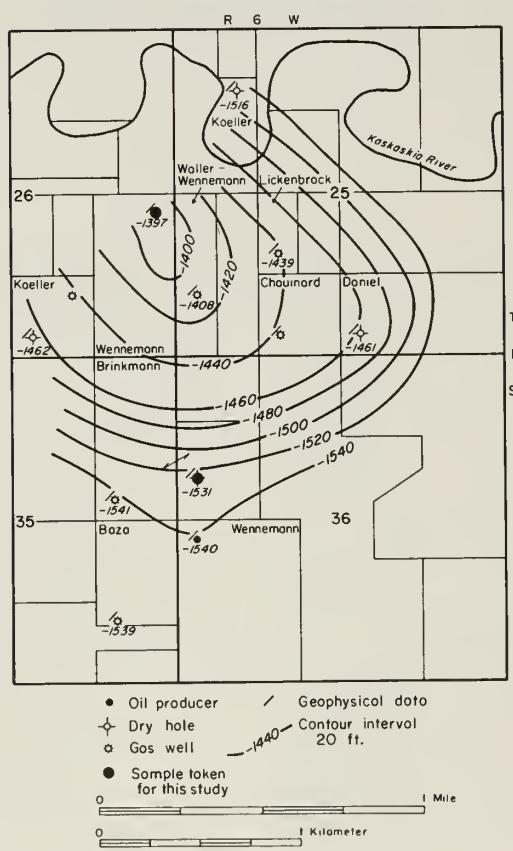


Fig. 5 - Structure map of the St. Libory gas field drawn on top of the Silurian reef.

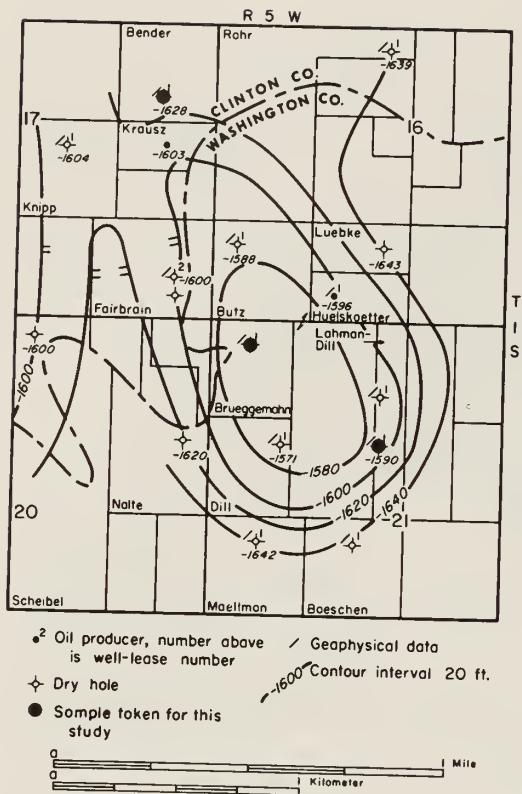


Fig. 6 - Structure map of the New Memphis South field drawn on top of the Silurian reef.

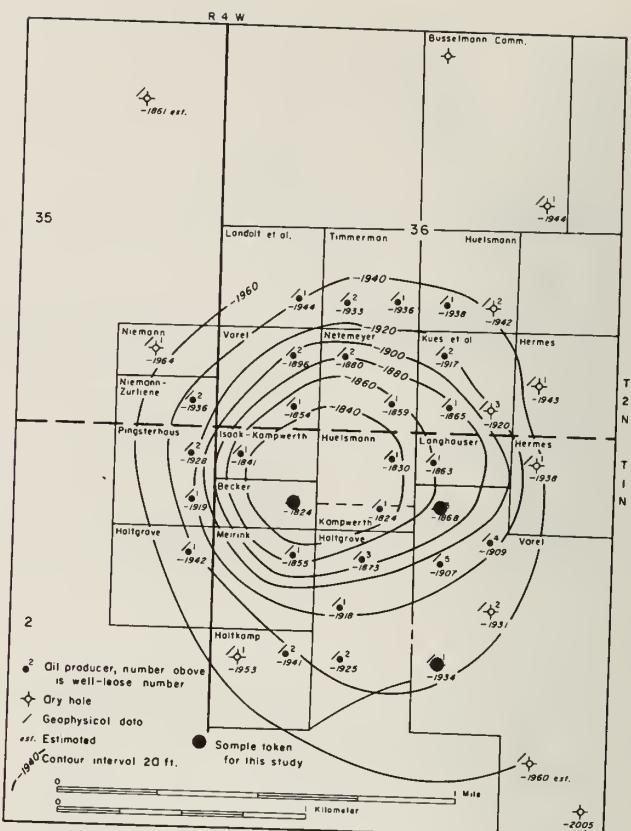


Fig. 7 - Structure map of the Germantown East field drawn on top of the Silurian reef.

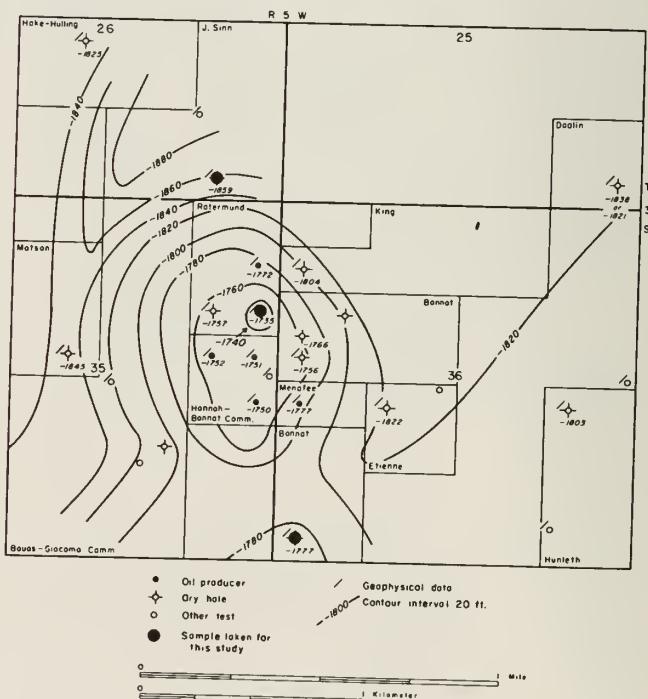


Fig. 8 - Structure map of the Coulterville North field drawn on top of the Silurian reef.

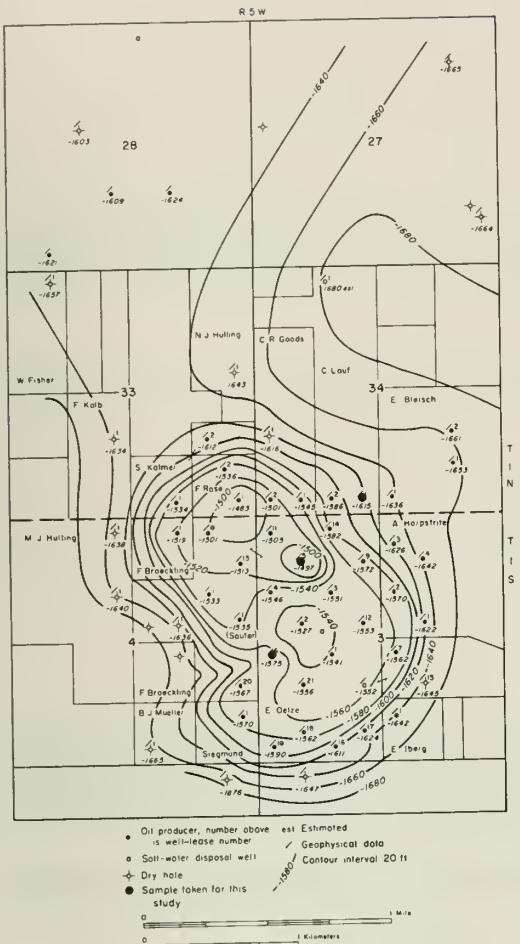


Fig. 9 - Structure map of the New Memphis field drawn on top of the Silurian reef.

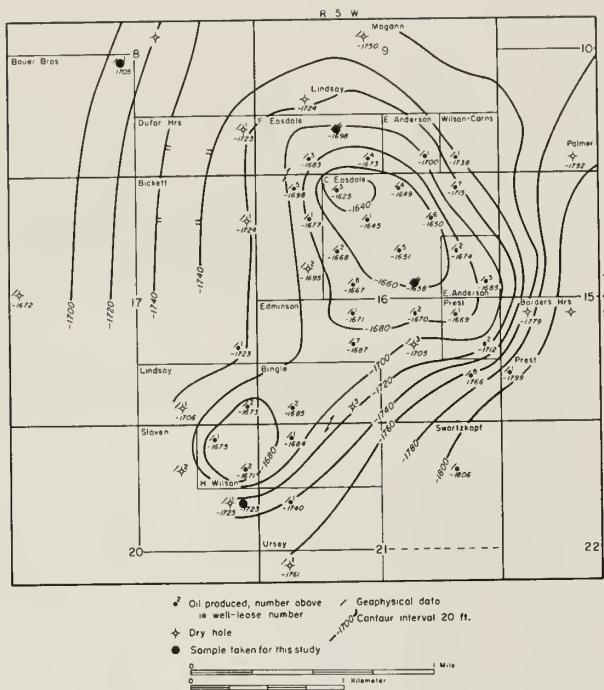


Fig. 10 - Structure map of the Tilden field drawn on top of the Silurian reef.

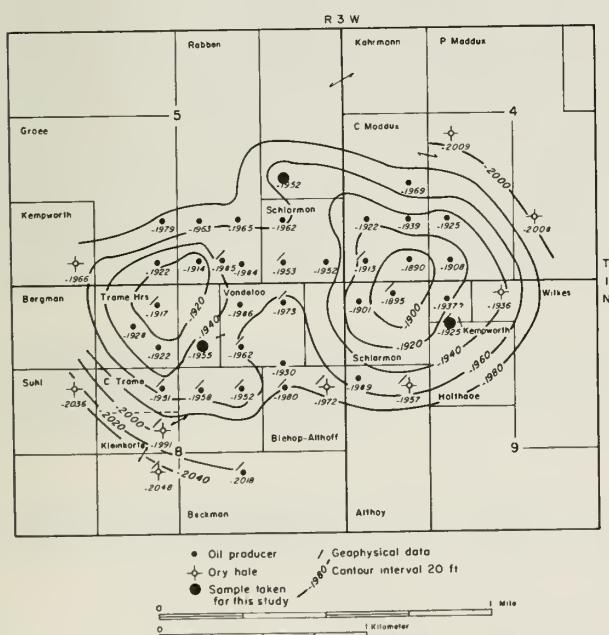


Fig. 11 - Structure map of the Bartelso field drawn on top of the Silurian reef.

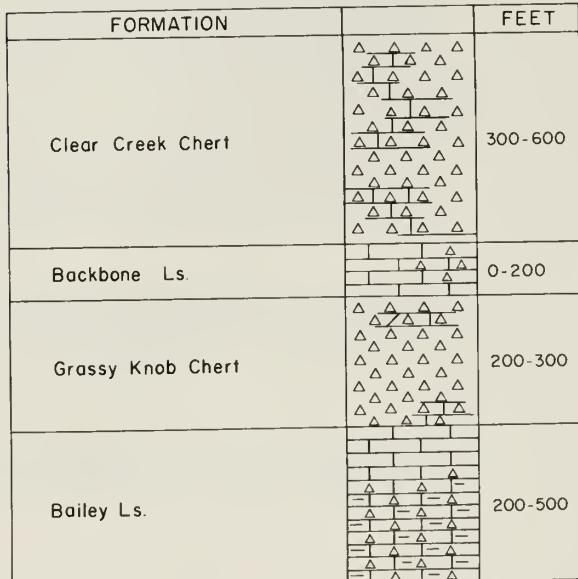


Fig. 12 - Columnar section of the Lower Devonian Series.

8	C-4428	NW SE SW 9-4S-5W, Randolph County	2219	Reef rock
16	R-11854	NE SE 26-1S-6W, St. Clair County	1813	Reef rock
	R-11855	NE SW 15-2S-5W, Washington County	2274	Limestone
62	R-11856	NE SW 15-2S-5W, Washington County	2274	Limestone
35	R-11856	WI / 2 SW NW 36-1S-6W, St. Clair County	1960	Dolomite
35	R-11857	WI / 2 SW NW 36-1S-6W, St. Clair County	2055	Reef rock
17	R-11858	NE SE 36-3S-6W, St. Clair County	0	Reef rock
17	R-11858	NE SW NE 10-3S-7W, Washington County	2237	Reef rock
18	R-11859	NE SW NE 10-3S-7W, Washington County	2237	Reef rock
18	C-6986	SW NW 31-3S-5W, Washington County	2086	Limestone
36	C-7153	SW NW 31-3S-5W, Washington County	0	Touching
19	C-8958	SW corner NE 23-2S-6W, St. Clair County	1872	Reef rock
20	C-9148	NW SE NW 23-2S-6W, St. Clair County	1879	Reef rock
63	C-9790	SE corner 28-3S-6W, St. Clair County	1840	Limestone
37	C-9861	NE NW NE 30-2S-3W, Washington County	2700	Limestone
46	C-9863	SE SE SW 30-2S-3W, Washington County	2715	Limestone
21	C-9868	NE NW SW 20-2S-3W, Washington County	2565	Reef rock
22	C-8958	SW corner NE 23-2S-6W, St. Clair Co.	1872	Reef rock

poroid

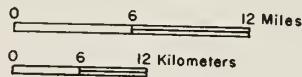
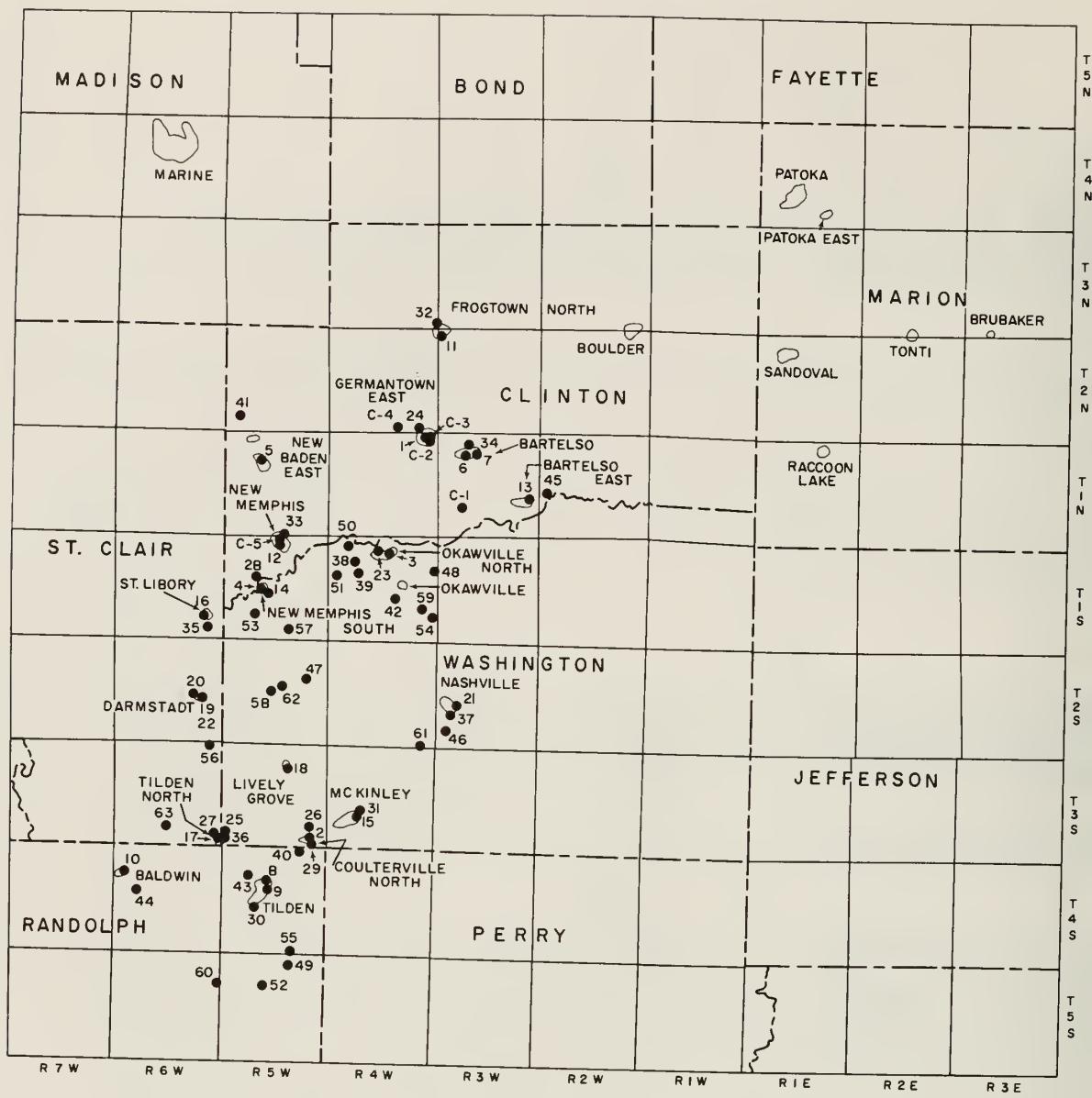


Fig. 13 - Sample index map.

TABLE 2 - LOCATION AND DEPTH INTERVAL OF 19 SAMPLES
FROM 5 INDIVIDUAL CORES

Core Index No.	Anal. Lab. No.	Sample Location	Distance from reef (miles)	Depth (ft)	Rock type
C-2758	R-12708	SW NE NW 29-1N-3W, Clinton County	3.5	2478	Dolomitic limestone
C-2758	R-12709	SW NE NW 29-1N-3W, Clinton County	3.5	2503	Dolomitic limestone
C-2758	R-12710	SW NE NW 29-1N-3W, Clinton County	3.5	2527	Dolomitic limestone
C-2758	R-12711	SW NE NW 29-1N-3W, Clinton County	3.5	2548	Dolomitic limestone
C-2957	R-12712	NW NW SE 1-1N-4W, Clinton County	Touching	2384	Dolomitic limestone
C-2957	R-12713	NW NW SE 1-1N-4W, Clinton County	Touching	2402	Dolomitic limestone
C-2957	R-12714	NW NW SE 1-1N-4W, Clinton County	Touching	2423	Dolomitic limestone
C-3365	R-12715	SW NW NE 1-1N-4W, Clinton County	0	2323	Reef rock
C-3365	R-12716	SW NW NE 1-1N-4W, Clinton County	0	2352	Reef rock
C-3365	R-12717	SW NW NE 1-1N-4W, Clinton County	0	2381	Reef rock
C-3365	R-12718	SW NW NE 1-1N-4W, Clinton County	0	2410	Reef rock
C-3367	R-12719	NE NW SE, 34-2N-4W, Clinton County	1.5	2437	Dolomitic limestone
C-3367	R-12720	NE NW SE, 34-2N-4W, Clinton County	1.5	2459	Dolomitic limestone
C-3367	R-12721	NE NW SE, 34-2N-4W, Clinton County	1.5	2482	Dolomitic limestone
C-3367	R-12722	NE NW SE, 34-2N-4W, Clinton County	1.5	2505	Dolomitic limestone
C-3961	R-12723	SE NW NW 3-1S-5W, Clinton County	0	2164	Reef rock
C-3961	R-12724	SE NW NW 3-1S-5W, Clinton County	0	2186	Reef rock
C-3961	R-12725	SE NW NW 3-1S-5W, Clinton County	0	2207	Reef rock
C-3961	R-12726	SE NW NW 3-1S-5W, Clinton County	0	2229	Reef rock

RESULTS AND DISCUSSION

The initial work was done on 63 Silurian rock samples which are grouped into four categories according to their location. Group I (22 samples) is in the reef. Group II (15 samples) is touching or less than 0.5 mile (0.8 km) from a reef. Group III (9 samples) is near a reef, 0.5 to 1.5 miles (0.8 to 2.4 km). Group IV (17 samples) is far from a reef, more than 1.5 miles (2.4 km). An immediate concern for statistical treatment of the data was the small number of samples in Group III which possibly could have been placed in either Group II or IV. Table 3 lists the data for the initial 63 samples.

In a second phase of the study we investigated the vertical variation of trace elements within an individual core in Group I (2 cores), Group II (1 core), Group III (1 core), and Group IV (1 core). The data for 19 individual vertical samples are listed in table 4 along with the depth intervals that they represent.

The results of the 63 analyses were first placed into one of the four groups according to proximity of the samples to a known reef formation. The mean value for each element in each group is tabulated in table 5. Most trace elements are depleted in Group III with the exception of calcium, sulfur, and arsenic. The

differences between means for Groups II, III, and IV are not very distinct and often are rather uniform, such as those for europium, samarium, lanthanum, gallium, and sodium.

Scatter plots were made for each element to further establish whether or not any trends were apparent between Groups II, III, and IV. Figure 14 illustrates scatter plots for lanthanum and manganese, again showing little clear-cut distinction between the three nonreef groups. This lack of distinction is especially apparent for lanthanum, while for manganese no clear distinction is made between any of the groups.

Linear correlations were computed for each individual group and then for all the samples to establish a possible basis for determining which of the many elements analyzed would be most useful for further investigation. Several combinations of elements were tested to establish which group had either high positive or high negative correlations with respect to their geographic groupings. Most major constituents were discarded from consideration, since they all showed little relation to their geographical sites although all showed high correlations with one another; for example, the high-calcium samples were very low in silica and the high-silica samples were low in calcium. The elements which showed the highest positive correlations with each group of samples were Br, K, V, Mn, As, Ga,

TABLE 3—concluded

LAB. NO.	LA	AG*	SC	SM	EU	SB
R11832	2.7 PPM		0.82PPM	0.33PPM	0.07PPM	1.0 PPM
R11841	1.7 PPM		0.37PPM	0.23PPM	0.05PPM <	0.3 PPM
R11843	1.0 PPM		0.35PPM	0.10PPM	0.02PPM	0.59PPM
R11848	5.4 PPM		0.47PPM	0.59PPM	0.11PPM	1.4 PPM
R11849	2.6 PPM		0.4 PPM	0.28PPM	0.05PPM	0.28PPM
R11852	3.1 PPM		0.2 PPM	0.31PPM	0.06PPM <	0.2 PPM
R11853	2.8 PPM		0.18PPM	0.28PPM	0.06PPM <	0.1 PPM
R11854	3.1 PPM		0.19PPM	0.34PPM	0.06PPM	0.25PPM
R11807	2.4 PPM		1.24PPM	0.21PPM	0.04PPM	0.28PPM
R11817	1.6 PPM		0.44PPM	0.15PPM	0.03PPM <	0.1 PPM
R11820	2.8 PPM		0.58PPM	0.37PPM	0.09PPM	0.25PPM
R11822	0.98PPM		0.23PPM	0.11PPM	0.02PPM	0.12PPM
R11823	0.42PPM		0.10PPM	0.04PPM	4 PPB	0.20PPM
R11827	2.3 PPM		0.3 PPM	0.22PPM	0.04PPM	0.12PPM
R11828	0.84PPM		0.19PPM	0.09PPM	0.02PPM <	0.06PPM
R11855	1.8 PPM		0.24PPM	0.22PPM	0.04PPM	0.13PPM
R11858	3.7 PPM		0.87PPM	0.41PPM	0.08PPM	0.55PPM
R11859	1.1 PPM		0.47PPM	0.10PPM	0.01PPM <	0.2 PPM
R11861	0.75PPM		0.2 PPM	0.09PPM	0.01PPM	0.22PPM
R11862	1.9 PPM		0.46PPM	0.18PPM	0.03PPM <	0.2 PPM
R11866	0.72PPM	<	0.1 PPM	0.08PPM	0.01PPM	0.23PPM
R11867	2.2 PPM		0.26PPM	0.20PPM	0.04PPM	0.18PPM
R11830	13 PPM		0.96PPM	1.57PPM	0.29PPM <	0.1 PPM
R11831	12 PPM		1.7 PPM	1.4 PPM	0.30PPM <	0.1 PPM
R11834	13 PPM		4.5 PPM	1.3 PPM	0.28PPM	1.2 PPM
R11840	14 PPM		1.4 PPM	1.6 PPM	0.34PPM	1.9 PPM
R11846	7.6 PPM		0.76PPM	0.82PPM	0.18PPM	0.47PPM
R11805	12.7 PPM		2.1 PPM	1.7 PPM	0.35PPM	0.20PPM
R11810	7.7 PPM		0.91PPM	0.76PPM	0.16PPM	0.19PPM
R11812	13 PPM		3 PPM	1.3 PPM	0.27PPM <	0.1 PPM
R11813	19 PPM		2.8 PPM	1.7 PPM	0.38PPM	0.53PPM
R11814	8.4 PPM		3.0 PPM	1.3 PPM	0.25PPM	0.14PPM
R11818	3.3 PPM		0.2 PPM	0.38PPM	0.07PPM	0.25PPM
R11826	22 PPM		1.9 PPM	2.1 PPM	0.49PPM	0.17PPM
R11857	11 PPM		2.7 PPM	1.4 PPM	0.30PPM <	0.1 PPM
R11860	8.2 PPM		1.5 PPM	0.99PPM	0.20PPM <	0.2 PPM
R11864	13 PPM	<	0.2 PPM	1.6 PPM	0.31PPM	0.37PPM
R11836	14 PPM		1.4 PPM	1.3 PPM	0.27PPM <	0.2 PPM
R11839	17 PPM		1.5 PPM	1.7 PPM	0.35PPM	1.1 PPM
R11842	9.5 PPM		1.3 PPM	1.0 PPM	0.22PPM	1.1 PPM
R11844	10 PPM		1.6 PPM	1.3 PPM	0.25PPM	0.41PPM
R11806	11 PPM		1.6 PPM	1.1 PPM	0.26PPM	0.15PPM
R11809	8.6 PPM		1.7 PPM	0.9 PPM	0.20PPM	0.25PPM
R11821	9.9 PPM		3.1 PPM	1.2 PPM	0.24PPM	0.38PPM
R11824	7.9 PPM		1.5 PPM	1.1 PPM	0.22PPM <	0.2 PPM
R11865	15 PPM		1.1 PPM	1.5 PPM	0.33PPM <	0.1 PPM
R11833	9.1 PPM		0.44PPM	1.0 PPM	0.24PPM <	0.2 PPM
R11835	8.1 PPM		1.1 PPM	0.80PPM	0.17PPM	0.32PPM
R11837	22 PPM		1.6 PPM	2.0 PPM	0.42PPM	1.1 PPM
R11838	9.8 PPM		1.3 PPM	1.1 PPM	0.21PPM <	0.3 PPM
R11845	17 PPM		2.7 PPM	1.6 PPM	0.38PPM <	0.1 PPM
R11847	14 PPM		2.0 PPM	1.6 PPM	0.30PPM <	0.1 PPM
R11850	11 PPM		0.46PPM	1.3 PPM	0.26PPM	0.41PPM
R11851	8.2 PPM		0.98PPM	0.70PPM	0.14PPM	0.34PPM
R11808	15 PPM		1.7 PPM	1.8 PPM	0.35PPM	0.24PPM
R11811	13 PPM		8.6 PPM	1.7 PPM	0.38PPM	1.2 PPM
R11815	11 PPM		1.5 PPM	1.1 PPM	0.25PPM	0.19PPM
R11816	6.2 PPM		0.63PPM	0.67PPM	0.14PPM	0.11PPM
R11819	10.9 PPM		2.4 PPM	1.1 PPM	0.25PPM	0.21PPM
R11825	11 PPM		1.2 PPM	1.3 PPM	0.26PPM	0.12PPM
R11829	10 PPM		1.1 PPM	1.0 PPM	0.22PPM	0.10PPM
R11856	13 PPM		3.8 PPM	1.4 PPM	0.29PPM <	0.2 PPM
R11863	11 PPM		1.5 PPM	1.3 PPM	0.29PPM <	0.2 PPM

* ALL MISSING VALUES WERE BELOW THE LIMITS OF DETECTION. APPROXIMATE L/D- AG: 1 PPM.

TABLE 5 - MEAN VALUES OF SILURIAN ROCK SAMPLES

Element	Group I (22)	Group II (15)	Group III (9)	Group IV (17)
Al (%)	0.73	1.49	2.89	1.72
Br	1.25	4.48	3.36	2.11
Ca (%)	48.7	33.6	36.8	41.59
Fe (%)	0.38	0.76	1.89	0.71
P (%)	0.021	0.023	0.030	0.033
K (%)	0.073	0.44	0.30	0.34
Si (%)	5.84	17.02	19.55	12.31
Ti (%)	0.019	0.083	0.12	0.056
V	14.1	29.7	20.4	23.2
Mg (%)	3.00	9.60	4.49	5.11
Mn	186	374	360	404
Na (%)	0.26	0.22	0.25	0.30
S (%)	0.12	0.095	0.076	0.092
As	1.09	0.78	0.55	0.61
Ga	0.34	1.37	1.28	1.26
La	2.12	12.12	11.82	12.33
Sc	0.39	1.87	1.67	1.93
Sm	0.22	1.37	1.28	1.31
Eu	0.04	0.28	0.26	0.27
Sb	0.32	0.40	0.43	0.31
Hg	0.21	0.53	0.64	0.32

La, Sc, and Hg. Table 6 gives correlations observed between all the samples. Several elements have a very high degree of correlation, especially the rare earth elements which have similar geochemical properties.

A Parks cluster analysis program (Parks, 1966), based in part upon correlation coefficients, was then computed to attempt to separate the samples into similar populations. Clusters were computed using several combinations of elements. The cluster using Ga, Br, As, La, K, and Sm is shown in figure 15. Ideally, the cluster analyses should indicate four distinct clusters or groups, corresponding to Groups I, II, III, and IV, although not necessarily in that order. Failing this, the three or fewer groups should show subgroupings corresponding more or less to the several groups. In our cluster analysis, although samples 1 to 22 (reef) were successfully grouped into one cluster along with sample 33, which

conceivably might be an unknown reef sample, the other three groups are randomly scattered through the large singular remaining cluster. This program was able to segregate reef from nonreef material but could not separate Groups II, III, and IV distinctly. Because it is highly possible that other factors such as percentages of clay, organic carbon, and carbonate carbon might be helpful in this matter, these factors will be included in future studies.

The data were subjected to discriminant analysis, and coefficients and centroids were obtained. Discriminant analysis (Bryan, 1951) is a statistical grouping technique which sets a predetermined number of groups (B_n) in which the coefficients (a_1, a_2, \dots, a_n) are adjusted to maximize the mathematical difference between B_a, B_b, \dots etc. according to the equations:

$$a_1 b_{1a} + a_2 b_{2a} + a_3 b_{3a} + \dots + a_n b_{na} = B_a$$

$$a_1 b_{1b} + a_2 b_{2b} + a_3 b_{3b} + \dots + a_n b_{nb} = B_b$$

The terms b_{1a}, b_{2a}, \dots are elemental concentrations of selected elements. In this statistical treatment individual samples were then withdrawn from the main block of data, and an attempt was made to classify them according to the original discriminant. For Br, K, Ga, Hg, La, and Sm, the results are shown in table 7. This attempt, while far from perfect, succeeded in correctly classifying all of the reef samples (Group I), with all but one indicating a probability of 99+ percent. Ten of the 15 samples from Group II were classified correctly, three incorrectly, and two ambiguously. The ambiguity, however, arose out of confusion with the Group III classification, which might be more nearly the correct classification in those cases. Group III, a set of only nine samples statistically rather insignificant, contained only three correctly classified members. Four classified as Group IV, and two as ambiguities. Group IV (17 samples) contained 15 correct and two ambiguous samples. Many that were correctly classified showed high degrees of probability (75 percent or above) but not as high as for the reef samples.

The preliminary investigation of vertical distribution of trace elements within several cores (see table 4) added little information other than to indicate some potential problems. The reef and nonreef cores can

clearly be separated (probably due to variations in clay and carbonate); however, the range of elemental concentrations varies much more for the nonreef cores than for the reef cores, as might be expected. These data point out the need for further extensive investigations of the area and the importance of carefully choosing samples for analysis and testing.

This empirical method of classification looks promising for additional study, but several modifications of it should be explored. Other factors such as percentages of clay and carbonate, along with analysis of acid-extracted portions must be considered. A statistically larger set of samples is necessary to enable the discriminant to be more selective. The geographic interval should be adjusted or reevaluated, or the number of intervals reduced by combining Groups II and III. Finally, other elements not analyzed in this study should be characterized.

as indicators of ore deposits and past geological conditions. Although many studies have been made on the geochemistry of trace elements (Boyle, 1974), very little is known about them. Numerous factors may account for the ability of several trace elements to serve as indicators of reef structures. Among them are: concentration by biological processes, adsorption of ions in clay or pore structures, properties and composition of the ground water, weathering processes, depositional patterns and composition of the overlying strata, and others. Speculation on the geochemistry of an individual element or group of elements is at best difficult and was not the primary goal of this initial study. Future efforts will include an attempt to resolve some of these fundamental questions through gathering and statistically evaluating considerable analytical data.

CONCLUSION

Reef and nonreef material can thus be differentiated on the basis of trace element data. This method can be used to supplement conventional paleontologic and geologic identification of reef structures.

The capacity of the technique to predict the location of a particular sample in relation to a known or unknown reef is less certain. Discriminant function analysis shows great promise even considering the relatively small number of samples studied. The analysis of more samples would greatly increase the reliability of any predictions made of the location of unknown reefs. Further studies will also include additional statistical techniques.

Although the relationship between Silurian reefs and petroleum accumulation cannot always be assumed, numerous petroleum deposits have been associated with reef structure acting as either a source or reservoir rock. Because the trace element distribution patterns observed in the oils may give an indication of their source, the analysis of oils associated with reef and nonreef structures for trace elements is an area demanding further investigation.

Why particular elemental associations seem to have the ability to differentiate reef and nonreef material is a difficult question. Trace elements have often been investigated

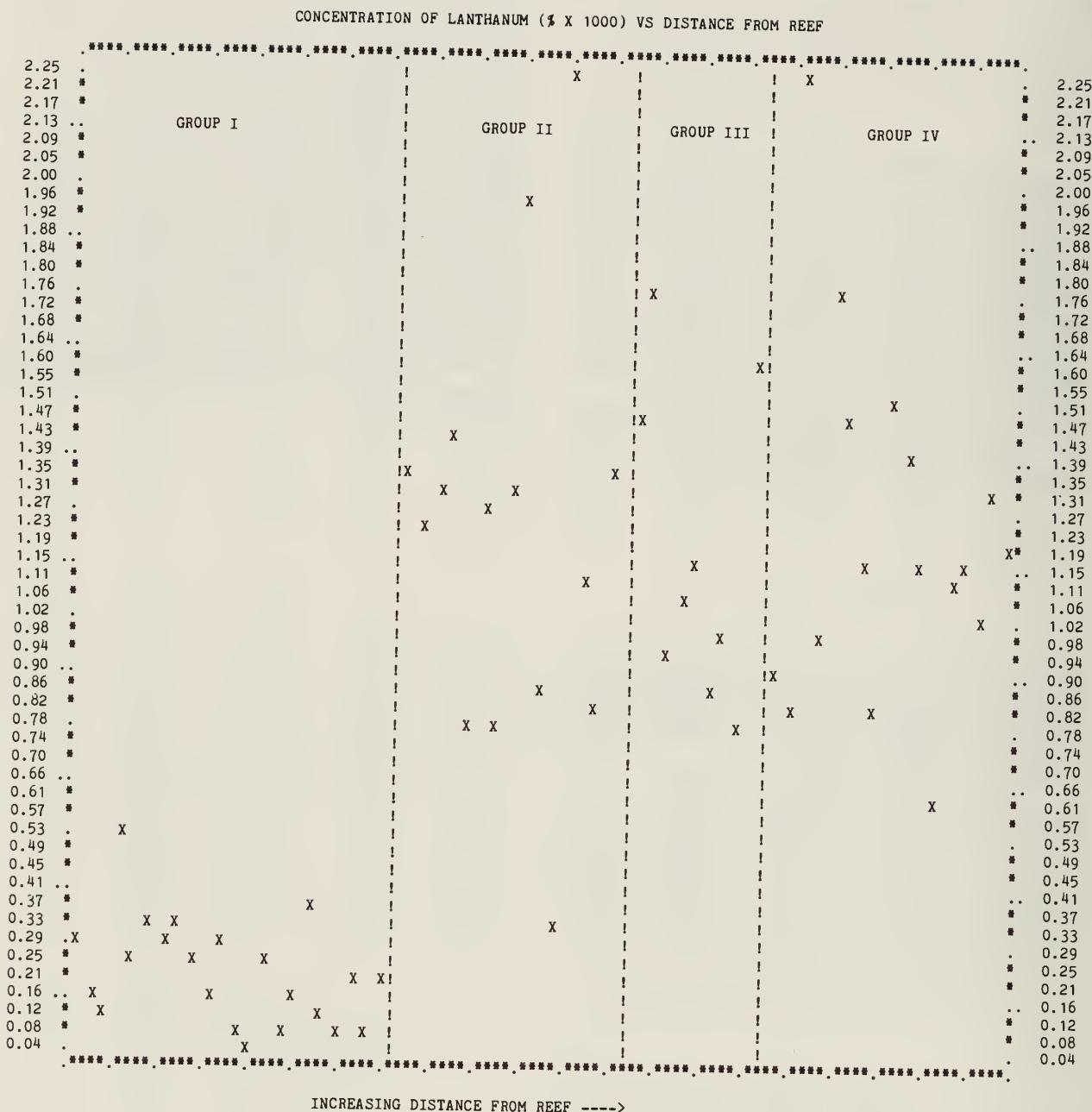


Fig. 14 - Scatter plots of Silurian rock samples. (A) Lanthanum. (B) Manganese.

PLOT OF MANGANESE CONCENTRATION (% X 100) VS DISTANCE FROM REEF

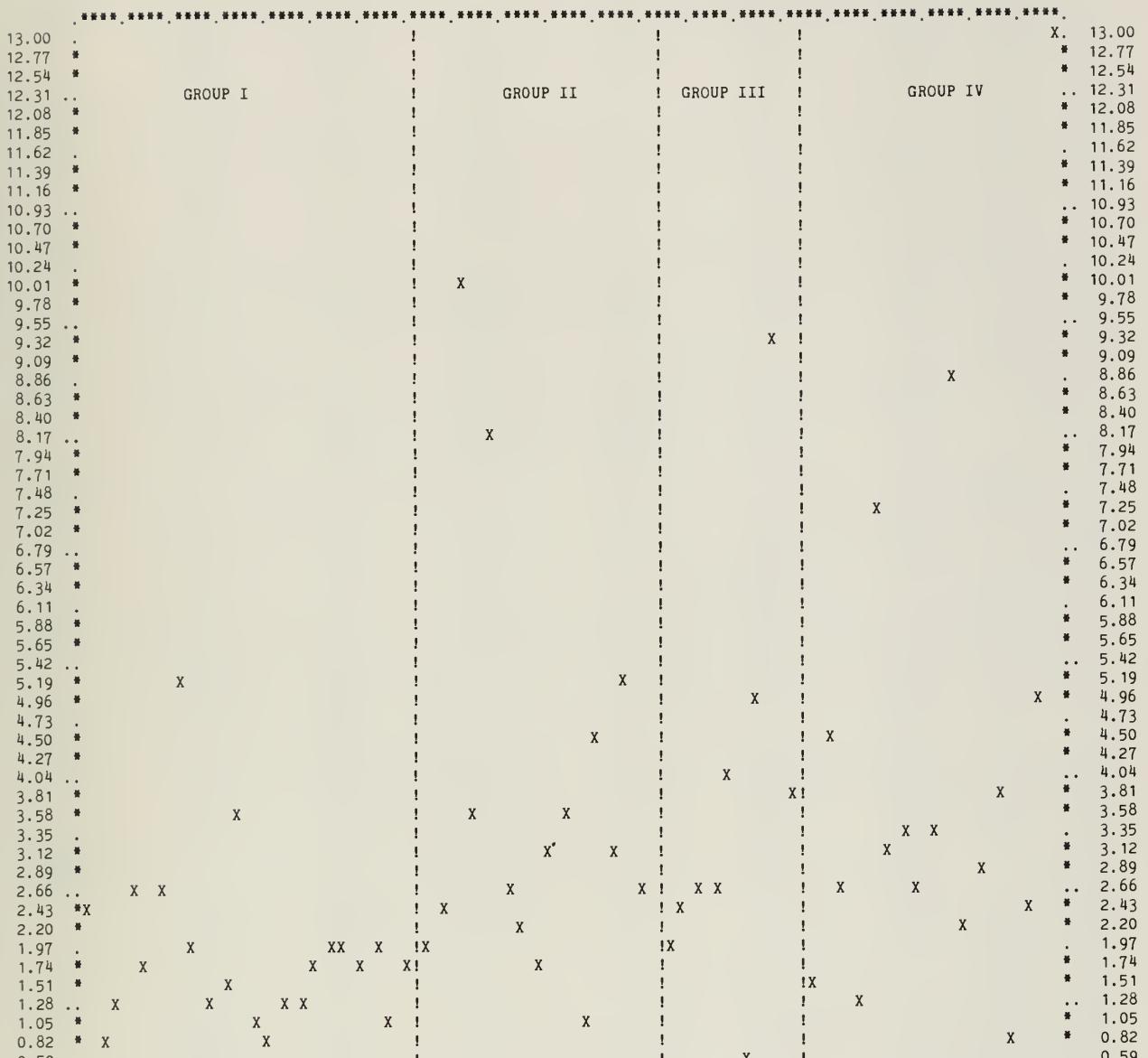


Fig. 14B

VALUE OF COEFFICIENT

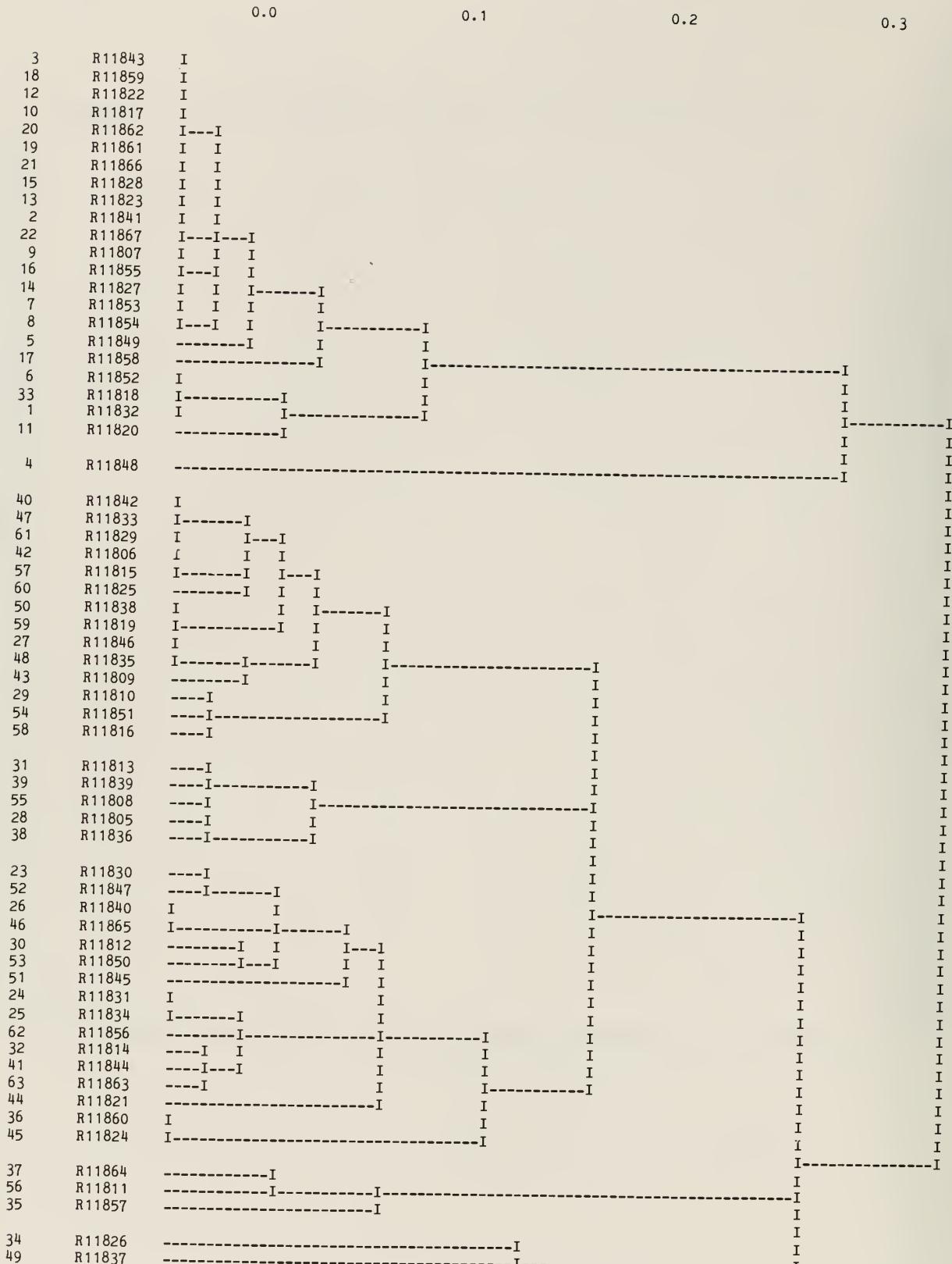


Fig. 15 - Cluster analysis of 63 samples using Br, K, As, Ga, La, and Sm.

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