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MINERALOGY OF ANTRIM SHALE, MICHIGAN

Topical Report

by

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ABSTRACT

Semi-quantitative x-ray mineralogical determinations were made for 12 surface, 104 core, and 707 samples from oil well cuttings distributed throughout the Michigan Basin. In addition, 15 samples that had undergone retorting were checked for mineralogical changes.

Gold, uranium, thorium, and rare-earth abundances were obtained for 22 samples from drill core at the Dow Chemical Company drill site in Sanilac County, Michigan.

Typical Antrim Shale is composed of 50-60% quartz, 20-35% illite, 5-10% kaolinite, 0-5% chlorite, and 0-5% pyrite. Calcite and dolomite, when present, are found mostly as limestone lenses or interbeds. Bedford Shale, which overlies the Antrim in eastern Michigan, has higher contents of total clays, illite, and kaolinite, and lower quartz contents. Ellsworth Shale, which grades laterally into Antrim in western Michigan, contains significant dolomite.

Antrim Shale from the southern and eastern margins of the Michigan Basin contains as much as 15% kaolinite, while samples from the northern, central and western portions contain up to 5% chlorite. Illite and quartz contents tend to be highest in the deepest part of the basin, where the Antrim is thickest.

The only mineralogical change that takes place during retorting is the loss of kaolinite diffraction peaks.

Uranium content increases upward to about 40 ppm and is greatest within shales of the Antrim. Limestone interbeds contain up to about 9 ppm uranium. Highest uranium contents are found just beneath limestone inter-

beds and just beneath Bedford Shale. Thorium contents, on the other hand, tend to be uniformly 10-12 ppm in Antrim Shale and up to 4 ppm in limestone interbeds.

Gold contents range up to about 0.05 ppm in Antrim Shale and 0.01-0.02 ppm in limestone interbeds.

Rare-earth abundances in Antrim Shale are lower than average North American shales. In the case of most rare earth elements, the overlying Bedford Shale has higher contents of most rare-earth elements.

INTRODUCTION

At present, there is considerable research being conducted in the United States on Upper Devonian-Lower Mississippian black, hydrocarbon-bearing shales as alternate sources of liquid and gaseous hydrocarbons. In Michigan this work is funded by the Department of Energy through Dow Chemical Company as principal contractor. These shales are widespread in the eastern portion of the United States and southern Ontario, Canada, and therefore, in total, contain enormous quantities of hydrocarbons. In states neighboring Michigan, these shales are called Ohio, Chattanooga, and New Albany; in the Michigan Basin, Upper Devonian black shale is called Antrim Shale.

That the Upper Devonian shales have a considerable content of liquid and gaseous hydrocarbons and combustible bituminous matter has been known for more than a hundred years. The Geological Survey of Canada (1863, p. 784) described an early attempt to exploit these shales for oil near Collingwood, Ontario:

> "In 1859, works for obtaining these oils were erected on the locality of this shale -- the shale, broken into small fragments was heated for two or three hours -- it is said from thirty to thirty-six tons of shale were distilled daily and made to yield 250 gallons of crude oil, corresponding to about 3 percent of the rock."

Lane (1903) reported 6.025% volatile carbon and 3.95% fixed carbon in Antrim Shale from a well in Barry County, Michigan.

Smith (1912, p. 259) stated:

> "In any case, the amount of oil in the Antrim Shale alone forms a reserve practically inexhaustible which can be drawn with exhaustion of the oil fields of the country."

The Dow Chemical Company's interest in oil shales began as early as 1955, when research planners suggested that underground processes, including in situ retorting, be studied. Their interest soon focused on the Antrim Shale, because of its proximity to their plants at Midland, Michigan. A summary of Dow's early research into energy from Antrim Shale was published by Matthews and Humphrey (1977).

In Michigan this most recent research program was begun in 1977, to test the feasibility of in situ burning of the shale to produce liquid and gaseous hydrocarbons, byproducts that might be used as fuel for, say, a low pressure gas-driven turboelectric plant. The entire program is quite comprehensive, some involved with field tests and others with laboratory studies. The study with which this paper deals concerns the determinative mineralogy portion of the shale characterization program, and the stratigraphic and regional variations and includes determining changes in mineral compositions and properties that take place during experimental retorting of shale samples.

The mineralogical characterization of the Antrim Shale is complicated by the fact that the Antrim Shale is known to vary in lithology across the Michigan Basin, reflecting primary environmental differences. Therefore, an important aspect of shale characterization is the determination of geographic variables.

The Antrim Shale is overlain by the Bedford Shale in the eastern portion of the Basin. Toward the west, the upper Antrim interfingers or otherwise merges with the lower portion of the Ellsworth Shale. In western Michigan, the interfingering facies relationship between the Ellsworth and Antrim is well known and in the central portion of the basin the Sunbury and Bedford Shales of Mississippian age overlie the Antrim. Ells (1978), as an important part of the shale characterization program, has prepared a

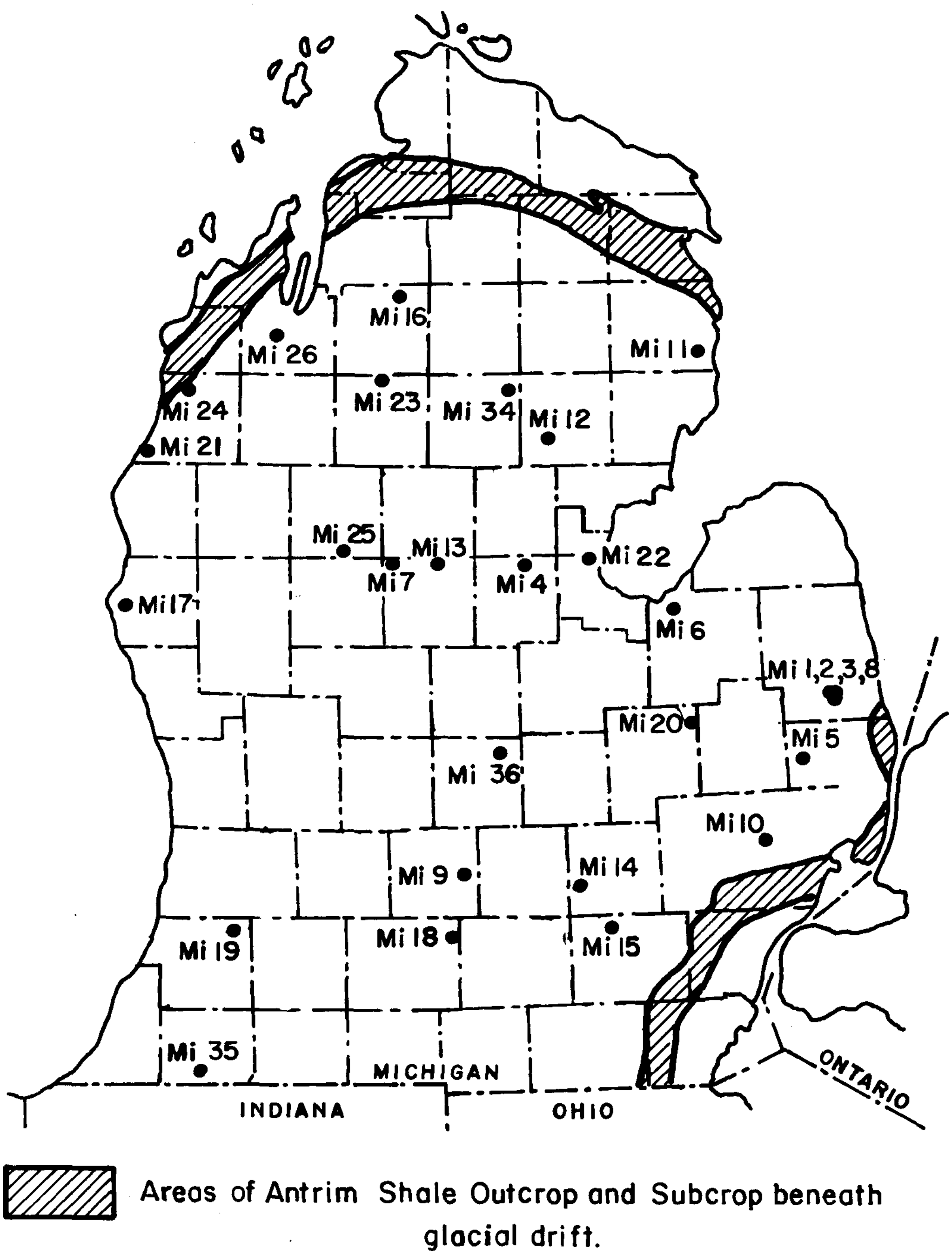

Figure 1. Locations of wells and Antrim outcrops.

number of stratigraphic cross sections of Devonian and Mississippian rocks, based on gamma ray signatures, and his cross sections show the general regional stratigraphic relationship among these important rock units.

GEOLOGIC SETTING OF ANTRIM SHALE

The Antrim Shale crops out along a circular band that roughly follows the outline of Michigan's Lower Peninsula (Fig. 1) and also occurs in portions of extreme northern Indiana, northwestern Ohio, and southern Ontario, Canada. The Antrim has been correlated with the New Albany Shale of Indiana (Lineback, 1968), the Ohio Shale of Ohio, and the Chattanooga Shale of the east-central United States. The Antrim has been considered Upper Devonian (Ells, 1978) and Lower Mississippian (Asseez, 1969) in age. Weller et al. (1948) and McGregor (1954) placed the Devonian-Mississippian boundary in the middle of the Antrim.

In Michigan, the Antrim Shale is underlain by Traverse Group formations, which consist of fossiliferous marine limestones and shales. At the type localities in Alpena and Presque Isle Counties, the Traverse Group is about 400 feet thick.

At most localities the Squaw Bay Limestone, the uppermost formation of the Traverse Group, underlies the Antrim. The Squaw Bay Limestone is about 10 feet thick, and consists of brown crystalline limestone. Shales which immediately underlie the Squaw Bay Limestone are gray, dark gray or blue-gray in color and thus resemble Antrim; however, gamma ray responses are distinctly lower, probably indicating lower hydrocarbon content.

The Antrim Shale of western Michigan consists of gray to black calcareous shale with interbedded brown argillaceous limestones and dolomite in the lower part and grading to black carbonaceous shale in the upper part (McGregor, 1954). In eastern Michigan, the Antrim is dark gray to black, hard, carbonaceous shale with beds of calcareous gray shale and thin limestone and dolomite lenses. Limestone concretions are common near the base.

The upper portion of the Antrim Shale grades laterally westward into the lower portion of the Ellsworth Shale in western Michigan (Cohee, et al., 1951). The Ellsworth is greenish gray, silty and in part dolomitic, and contains spore cases, glauconite, and pyrite concretions (McGregor, 1954), as well as oölites (Hale, 1941).

In eastern Michigan, the Antrim is overlain by the Bedford Shale which is gray, silty and sandy, and dolomitic in places. The Bedford is more sandy near its top, and appears to grade upward into the overlying Berea Sandstone.

MICHIGAN BASIN

The Michigan Basin is commonly called a structural basin and underlies all of the State of Michigan (except for the western Upper Peninsula), portions of northwestern Ohio, northern Indiana, extreme northeastern Illinois, and eastern Wisconsin, and southern Ontario, Canada. It is nearly circular in shape and covers more than 120,000 square miles.

The Michigan Basin contains rocks from Cambrian through Pennsylvanian and Jurassic age. The basin is covered by glacial drift up to 1000 ft. thick in places. There are a few outcrops of Antrim Shale at some scattered localities, mostly in the northern portion of the Lower Peninsula.

The deepest part of the Michigan Basin is in the Midland-Bay City area. Here, the Antrim is found at a depth of about 3,000 feet.

PURPOSE OF THE INVESTIGATION

The purpose of this investigation was to determine the semi-quantitative mineralogy of the Antrim Shale in cores and well cuttings, distributed across the Michigan Basin (Fig. 2). To this end, 104 semi-quantitative X-ray diffraction analyses have been done of samples taken from cores from wells MI-1, MI-2, and MI-3 at the Dow drill site in Sanilac County. Twelve are of outcrop samples, most from the Paxton Quarry, Alpena, Michigan. The others, some 707, are of cuttings obtained from 26 wells distributed throughout the Michigan Basin.

Some of the samples were re-analyzed after retorting to help determine whether changes in rock mechanical characteristics would correlate with mineralogical changes.

One suite of core samples of Antrim Shale from well MI-1 was analyzed for a number of elements including uranium and thorium by neutron activation at the Phoenix Memorial Laboratory of Ann Arbor. The same samples were used as standards to analyze another suite from wells MI-1 and MI-2 by gamma ray spectroscopy. Some polished and thin sections were examined microscopically to aid in mineral identification. This paper also incorporates data from the thesis by George Bennett (1978).

ANALYTICAL PROCEDURE

Sampling

A total of 29 wells were sampled (Fig. 1). The exact locations, well designations and operating companies are listed in Table 1. Core samples were sampled only from wells MI-1, MI-2 and MI-3 at the Dow Chemical Company's drill site in Sanilac County, Michigan. Material for mineralogical and chemical analysis were taken from trimmings immediately

TABLE 1

Wells Sampled for Antrim Oil Shale Project

Well Number	Company	Well Name & Number	Location
MI-1	Dow Chemical	Dow/ERDA 100	NE 8, 9N-15E
MI-2	Dow Chemical	Dow/ERDA 101	NE 8, 9N-15E
MI-3	Dow Chemical	Dow/ERDA 102	NE 8, 9N-15E
MI-4	Consumers Power	Marsh #1	NE 15, 16N-1E
MI-5	Mich. Cons. Gas	C. C. 770	SE 30, 7N-13E
MI-6	E. E. Brehm	Cosens 1-36	NE 36, 14N-7E
MI-7	Merrill Drlg.	L. Bazaire 2-5	SE 5, 16N-6W
MI-8	Dow Chemical	Dow/ERDA 105	NE 8, 9N-15E
MI-9	Kulka & Schmidt	Rounds-Jones 1-7	NW 7, 2N-3W
MI-10	Reef Petroleum	Smitha 4-1	NE 1, 3N-11E
MI-11	Elek & Bartlett	Schrade #1	SW 2, 25N-8E
MI-12	Marathon Oil	Baumchen K-6	NW 27, 22N-2E
MI-13	Hunt Energy	Wild 1-3	SE 3, 16N-4W
MI-14	Amoco	Patrick 1-28	NW 28, 2N-3E
MI-15	Hunt Energy	Weber 1-26	SW 26, 1S-4E
MI-16	Amoco	Fawcett 3-24	SW 24, 28N-6W
MI-17	Amoco	Tompkins 1-2	SE 2, 14N-18W
MI-18	Scott Drlg. Co.	Collier 1-12	NE 12, 2S-4W
MI-19	Kulka & Schmidt	Guldemond 1-21	SW 21, 1S-13W
MI-20	Crystal Expl.	Ulrich #1	NW 13, 9N-8E
MI-21	Aztec	State 3-2	SE 2, 21N-17W
MI-22	ATE-Dart-et al.	Broderick	NE 9, 16N-4E
MI-23	Dart	Bruggers 1-7	NW 7, 24N-6W
MI-24	Reef	Wussow 1-1	SW 1, 23N-15W
MI-25	Richard Beeson	Turner 1-17	NW 17, 17N-8W
MI-26	Northern Mi. Expl.	State Blair 3-21	NE 21, 26N-11W
MI-34	Sun Oil Company	St. Helen 15-35	SE 28, 24N-1W
MI-35	Vernon East	Woods #1	SE 18, 7S-14W
MI-36	Hunt Energy	Hebeler 1-9	NW 9, 7N-1W

adjoining the rock mechanical samples. For all other wells, samples consisted of cuttings, generally representing ten-foot intervals, provided by Core Laboratories.

All samples were submitted to the Institute of Mineral Research, Michigan Technological University, where they were pulverized to pass through a 325 mesh screen. These samples were split, with a portion being supplied for mineralogical analysis and a portion forwarded to the Department of Chemistry and Chemical Engineering, Michigan Technological University for chemical analysis.

Identification of Non-Clay Minerals

The minerals were studied by X-ray diffraction using a Philips recording diffractometer under the following operating conditions:

Target:	Copper
Detector:	Proportional Counter
Voltage:	40KV
Current:	20 ma
PHS:	Baseline: 1.5V, Window: 2.5V
Range:	500 cps
Time Consultant:	2 sec.
Goniometer Speed:	2°/min.

The procedures used in mineral identification are those described by Carroll (1970).

Quartz, pyrite, calcite, and dolomite can commonly be identified directly by visual inspection of drill core. The X-ray powder data for these four minerals are listed in Table 2.

TABLE 2

Powder X-ray Diffraction Data for Quartz, Calcite, Dolomite, and Pyrite

Quartz, Low JCPDS#5-490			Calcite JCPDS#5-586			Dolomite JCPDS#11-78			Pyrite JCPDS#6-710		
d,Å	I/I_1	hkl	d,Å	I/I_1	hkl	d,Å	I/I_1	hkl	d,Å	I/I1	hkl
4.26	35	100	3.86	2	102	4.03	<5	101	3.128	35	111
3.343	100	101	3.035	100	104	3.69	5	012	2.709	85	200
2.458	12	110	2.845	3	006	2.886	100	104	2.423	65	210
2.282	12	102	2.495	14	110	2.670	10	006	2.2118	50	211
2.237	6	111	2.285	18	113	2.540	10	015	1.9155	40	220
2.128	9	200	2.095	18	202	2.405	10	110	1.6332	100	311
1.980	6	201	1.927	5	204	2.192	30	113	1.5640	14	222
1.817	17	112	1.913	17	108	2.066	5	021	1.5025	20	230
1.801	<1	003	1.875	17	116	2.015	15	202	1.4448	25	321
1.672	7	202	1.626	4	211	1.848	5	024	1.2427	12	331
1.659	3	103	1.604	8	212	1.804	20	018	1.2113	14	420
1.608	<1	210	1.587	2	1.0.10	1.786	30	116	1.1823	8	421
1.541	15	211	1.525	5	214	1.781		009	1.1548	6	332
1.453	3	113	1.518	4	208	1.567	10	211	1.1057	6	422
1.418	<1	300	1.510	3	119	1.545	10	122	1.0427	25	511
1.382	7	212	1.473	2	215	1.496	1	1.0.10	1.0060	8	432
1.375	11	203	1.440	5	300	1.465	5	214	0.9892	6	521
1.372	9	301	1.422	3	0.0.12	1.445	5	028	0.9577	12	440
1.288	3	104	1.356	1	217	1.431	10	119	0.9030	16	600
1.256	4	302	+ 20 lines to 0.9655			1.413	5	125	0.8788	8	611
1.228	2	220				1.389	15	030	0.8565	8	620
+ 19 lines to 0.9285						1.335	10	0.0.12	0.8261	4	533
						+ 18 lines to 0.923			0.8166	4	622
									0.7981	6	631

Identification of Clay Minerals

Clay minerals present special problems in identification which arise from variations in degree of perfection of crystallinity, variations in chemical compositions, and the superposition of diffraction lines.

Kaolinite-Chlorite

The (001) diffraction for kaolinite (7.15Å) and (002) diffraction for chlorite (7.05Å) are superimposed. In order to resolve this, one of two tests can be used.

1. Heating to 550°C. At 550°C, the crystal structure of kaolinite collapses and becomes amorphous to X-rays, and thereby the interferring peak disappears. However, checks on the survival of known chlorite from Antrim Shale showed that it remained stable at 550°C, but there is a change in the intensities of (001) and (002) peaks like those observed in Brown (1961).

2. Acid treatment. Kaolinite is stable in nitric or hydrochloric acid solution of reasonable dilution (e.g. 3 N). Chlorite is unstable in acid solutions.

Crystallinity of Illite

Illite was first described by Grim (1937) as a mineral with 10Å basal spacing that does not expand when treated with ethylene glycol or glycerine, but a mineral that cannot be further identified as to mica type. Since that time, it has become clear that illite and montmorillonite commonly interstratify over a wide range of proportions of end members. In a rock such as Antrim Shale, the total quantity of illite, including any of it interstratified with montmorillonite, rarely exceeds 35 percent by weight of rock. Because illite is generally not the most abundant phase, and cannot be separated from an illite - montmorillonite phase by any simple mineralogical procedure, the interstratified phase is generally reported as "illite". The amount of interstratified montmorillonite can be estimated qualitatively in those cases in which it is substantial, from the asymmetry of the basal (10Å) illite diffraction point.

Chlorite

Chlorite can be identified easily in clay-bearing materials provided its content is not excessively high in iron. In most chlorites, the (001) diffraction peak (14Å) has an intensity of about 50-60% of the (002) diffraction peak (7Å). In high-iron clay chlorites, however, there is a marked decrease in intensity of the 14Å diffraction peak; indeed, in some iron-rich chlorites, there is no 14Å diffraction. The chlorites in the Antrim Shale appear to be typical chlorites in which the intensity of (001) is about 60%.

Kaolinite

Fairly pure samples of kaolinite can be studied for their degree of crystallinity, by means of measuring the intensities of the various diffraction peaks. However, in the Antrim Shale kaolinite rarely constitutes more than 10% of the rock by volume, and cannot be separated effectively. Therefore estimates of the degree of crystallinity cannot be made with a reasonable degree of confidence.

Semi-Quantitative Analyses

Semi-quantitative mineralogical analyses by means of X-ray diffraction (Renton, 1977) were made by Bennett (1978) through the use of prepared standards using a quartz matrix, and measuring the time for 10,000 counts.

Since these standards were made from commercial clays that differ to an unknown degree in crystallinity from the clays in the Antrim, the analyses are semi-quantitative at best. Nevertheless, this is a useful method of inter-sample comparison within the Antrim Shale, but not for a study of shales in general.

For the semi-quantitative study standard plots were made of percent quartz in sample as a function of $\frac{\text{peak height of mineral}}{\text{peak height of quartz + peak height of mineral}}$. The specific diffraction peaks are listed in Table 3.

Table 3

Diffraction Peaks Used in Semi-Quantitative Analyses

Mineral Ratio Sought	Quartz Peak Used	Other Mineral Peak Used
Quartz/illite	(100)	(002)
Quartz/kaolinite	(100)	(001)
Quartz/chlorite	(100)	(001)
Quartz/dolomite	(200)	(113)
Quartz/calcite	(200)	(023)
Quartz/pyrite	(200)	(311)

To determine the accuracy of the data 50 randomly chosen samples were analyzed twice and the results showed an agreement within ± 5% of the quantity contained. Plots of peak height ratios of standards are plotted against compositions in Fig. 2. Total quartz percent refers to the percentage of quartz in each set of prepared standards.

NEUTRON ACTIVATION ANALYSIS

Samples for neutron activation analysis were pulverized to pass through a 200 mesh screen. Samples of approximately 100 mg were split, carefully weighed and placed into pure silica glass tubes and sealed with a hydrogen-oxygen flame. Slow neutron activation analyses were obtained from the Phoenix Memorial Laboratory, University of Michigan.

The elements of primary interest were uranium, thorium, and gold. These elements were not to be analyzed by any other procedure. Analyses for other elements, including rare-earth elements, antimony, arsenic, selenium, silver, nickel, and cobalt were also obtained.

GAMMA-RAY SPECTROSCOPY

The gamma-ray spectroscopic method is the measure of natural gamma-ray emission from uranium, thorium, and other radioactive elements. The method used in this study was that described by Bunker and Bush (1966), which is based upon comparison with known standards. In this case the standards used were those used in neutron activation analysis. The standards contained 4.5 ppm, 28.0 ppm and 40 ppm U and 6.7 ppm, 12.8 ppm and 14.6 ppm Th.

Two hundred gram samples were sealed in 4 in. (diameter) by 1.5 in. cylinders. sealed with plastic tape, and stored for two weeks to allow Rn^{222} and Rn^{220} to equilibrate within the containers.

The radiometric analysis procedure of Johnson (1977) was used. The samples were placed on a NaI crystal shielded by 4" lead walls. A spectrum of 0-3 MEV was counted on a 400 channel pulse height analysis system. Backgrounds before the first sample and after last sample were averaged and subtracted from peak heights in subsequent calculations. A 400 minute counting interval was used.

Plots of counts/400 min/200 gr. versus concentrations in standards were straight lines for both uranium and thorium.

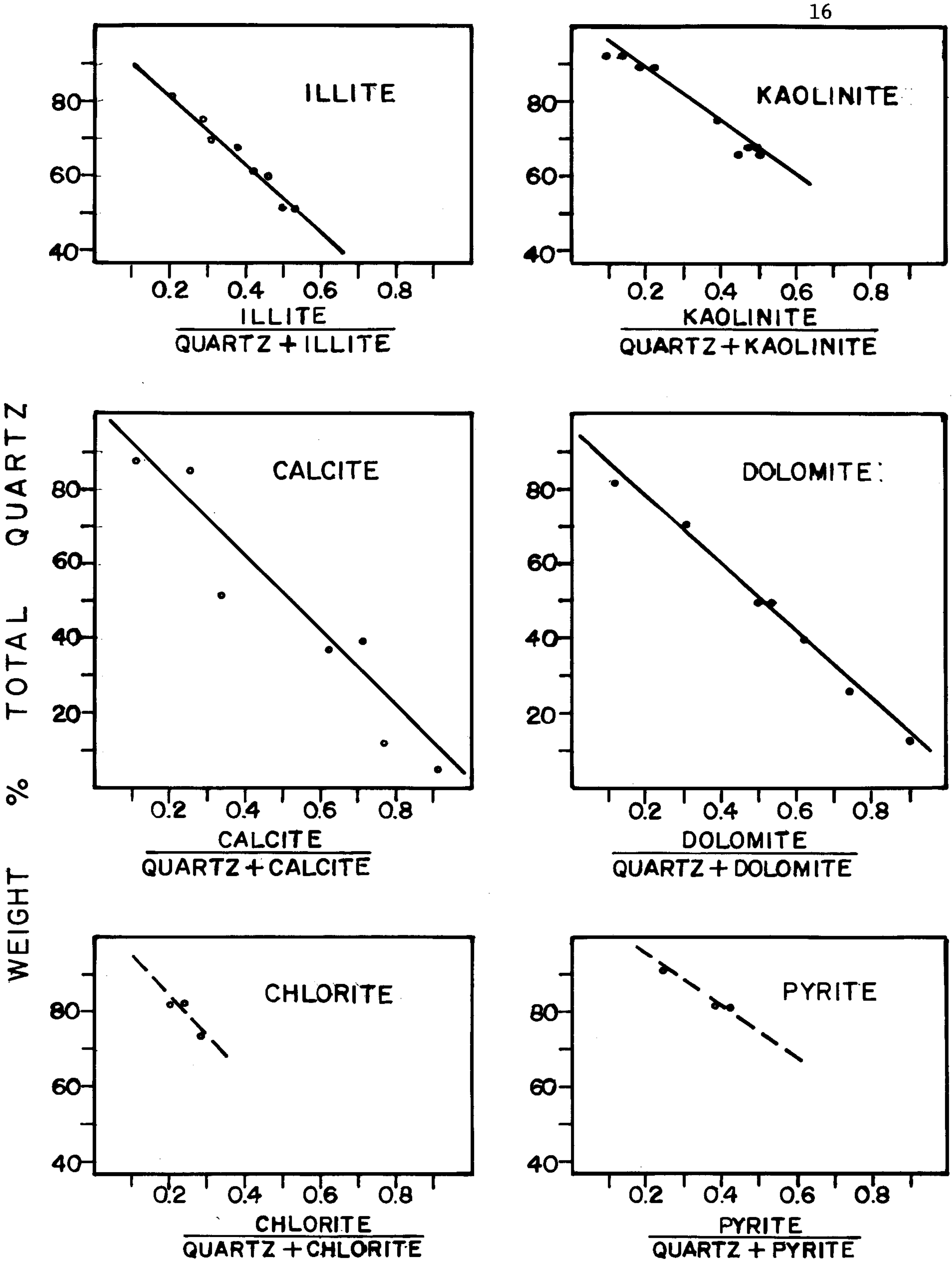

Figure 2. Standard curves for determination of ratios of quartz and other Antrim rock-forming minerals.

MINERALS PRESENT IN ANTRIM SHALE

Typical Antrim Shale is composed of 50-60% quartz, 20-35% illite, 5-10% kaolinite, 0-5% chlorite, and 0-5% pyrite. Dolomite and calcite, when present are found as limestone lenses or interbeds.

Quartz

Most quartz in Antrim Shale is in the silt to clay sized fractions. Thin section examination showed that only 20-40% by volume of quartz is in sizes resolvable with a light microscope. The smearing of organic material during preparation may have masked more of the resolvable quartz. Most of the quartz is probably detrital, but significant quantities could have precipitated from sea water or formed during diagenesis (Hathon, et al., 1980, Renton, 1977). Precipitated quartz is most important in the lower portion of the Antrim where it is associated with carbonates (Bennett, 1978).

Illite

Large (>0.1mm) individual flakes of muscovite probably detrital, can be seen in thin sections, recognizable by high birefringence and perfect basal cleavage. However, illite can also be seen, but no optical distinction was attempted in this study. The most abundant mica, as determined by X-ray analysis is one of poor crystallinity and is called "illite." SEM analyses by Bennett (1978) show that this illite contains significant iron. Bennett (1978) considered illite to be at least in part authigenic.

A rather wide variability can be seen in the asymmetry of the (001) reflection for illite. Such asymmetry is an indication of mixed layering of mica units and expansible smectite units.

Three examples of asymmetry are shown in Figure 3. MI-36, between 2310 ft. and 2320 (Fig. 3A), is the (001) reflection of illite with little or no smectite interlayers. MI-26, 1390-1400 ft. (Fig. 3B) is a typical example of illite from Antrim Shale, in which some interlayering is evident from the shoulder on the reflection. MI-26, 1410-20 ft. (Fig. 3C) shows an extreme example in which a smectite basal peak can be distinguished; however, ethylene glycol treatment does not expand that peak of 17Å, as it should if there were discrete smectite in the sample. Therefore, this is considered interstratified illite-smectite with a large percentage of smectite interlayers.

Kaolinite

Kaolinite typically makes up no more than 10% of Antrim Shale. As will be discussed later, kaolinite is more abundant in the eastern part of the Michigan Basin than in the western. The kaolinite content in overlying Bedford Shale in eastern Michigan by contrast is more than 20%.

Pyrite

Pyrite typically makes up 3-5% of Antrim Shale. It is most abundant in organic rich samples, and most if it occurs as framboids ranging in size from a few micrometers to 1mm in size. It also occurs as nodules up to 5 cm in diameter and as fracture fillings.

Carbonates

Calcite and dolomite are abundant in interbeds confined largely to the lower fourth of the Antrim Shale, and in the Ellsworth Shale. Calcite occurs largely as fossil debris in samples with abundant clastic material, and generally organic content. Nodules of carbonates are common at the base of the Antrim.

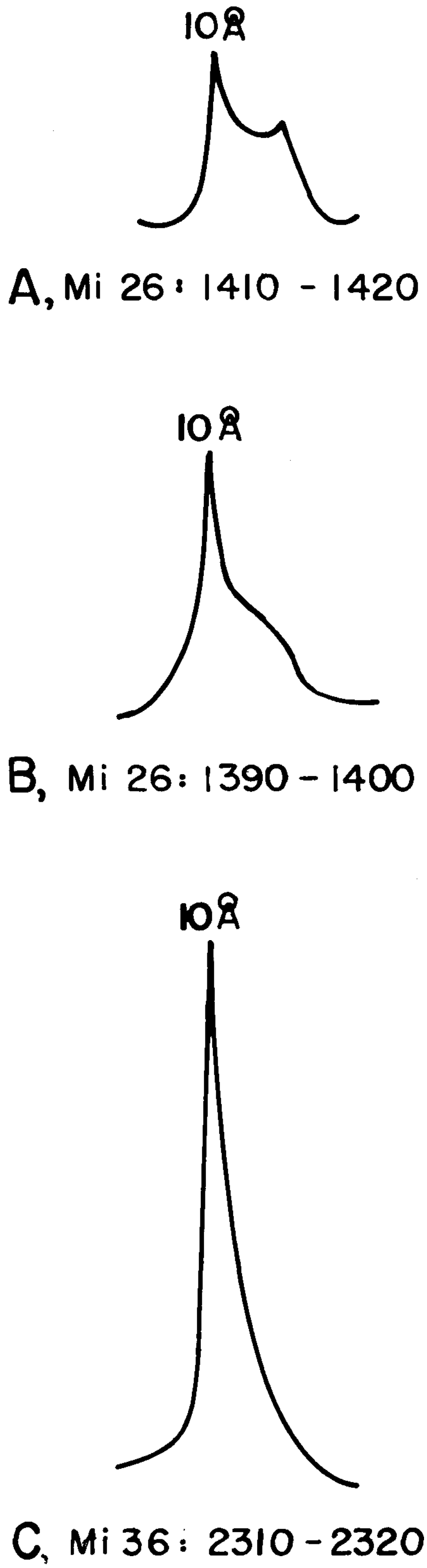

Figure 3. Variations in symmetry of illite 10Å basal X-ray diffraction peak caused by mixed layers of montmorillonite.

Chlorite

Chlorite is a minor mineral in Antrim Shale, generally making up 5% or less of the rock, but it is much more abundant in central or western Michigan than along the more kaolinitic, eastern portion of the Michigan Basin.

MINERALOGY OF ELLSWORTH SHALE

The Ellsworth Shale is known to interfinger with and grade into the upper portion of the Antrim Shale in western Michigan. Thin beds of "Ellsworth-like" shale in the Paxton Quarry, Alpena, are greenish-gray and silty. X-ray diffraction revealed substantial dolomite to be present. At Alpena, only minor "Ellsworth-like" interbeds, up to a few centimeters thick, are present in the Antrim; westward, the Ellsworth Shales gradually thicken at the expense of the Antrim.

In drill cuttings from western Michigan (eg. MI-19, 1160-1220; MI-23, 2500-2530; MI-17, 1550-1630, MI-25, 2940-3050) 25-40% dolomite is present. Dolomite percentages commonly range widely from sample to sample in cuttings, and probably is a reflection of relative thicknesses of Antrim to Ellsworth units as well as sampling techniques.

Chlorite is common in Ellsworth Shale. Occasionally, kaolinite may be present, but in very small amounts.

Illite contents range from 20-30% in Ellsworth Shale.

Quartz contents of Ellsworth Shale (up to 35% commonly) are generally lower than Antrim Shale.

MINERALOGY OF BEDFORD SHALE

In drill cores from the Dow Chemical Company drill site in Sanilac County, the Bedford Shale is easily distinguished from underlying Antrim by its reddish-brown color, and its tendency to part along thin beds.

Semi-quantitative X-ray mineralogy shows that Bedford Shale contains larger percentages of total clay minerals and correspondingly lower percentages of quartz. Moreover, the Bedford typically contains 15-20% kaolinite, as compared to 5-10% in Antrim Shale immediately below. The mineralogical changes can be easily picked out in wells MI-1, MI-2 (top Antrim = 1220') and MI-3 (top Antrim = 1225').

Quartz in the Bedford Shale is in grains ranging from silt to sand size. The grain size of quartz increases upward and grades into the overlying Berea.

MINERALOGY OF TRAVERSE GROUP ROCKS

The rocks of the Traverse Group that underly the Antrim Shale are sandy to shaly limestones with shale interbeds. Typically, as in the case of MI-1, 1450-1480, the calcite content ranges from 25-50%, quartz to 40%, and total clays 0-50%. Dolomite is commonly present but does not seem to form persistent beds. In some cases, for instance MI-2, 1450-60, dolomite is the essential constituent.

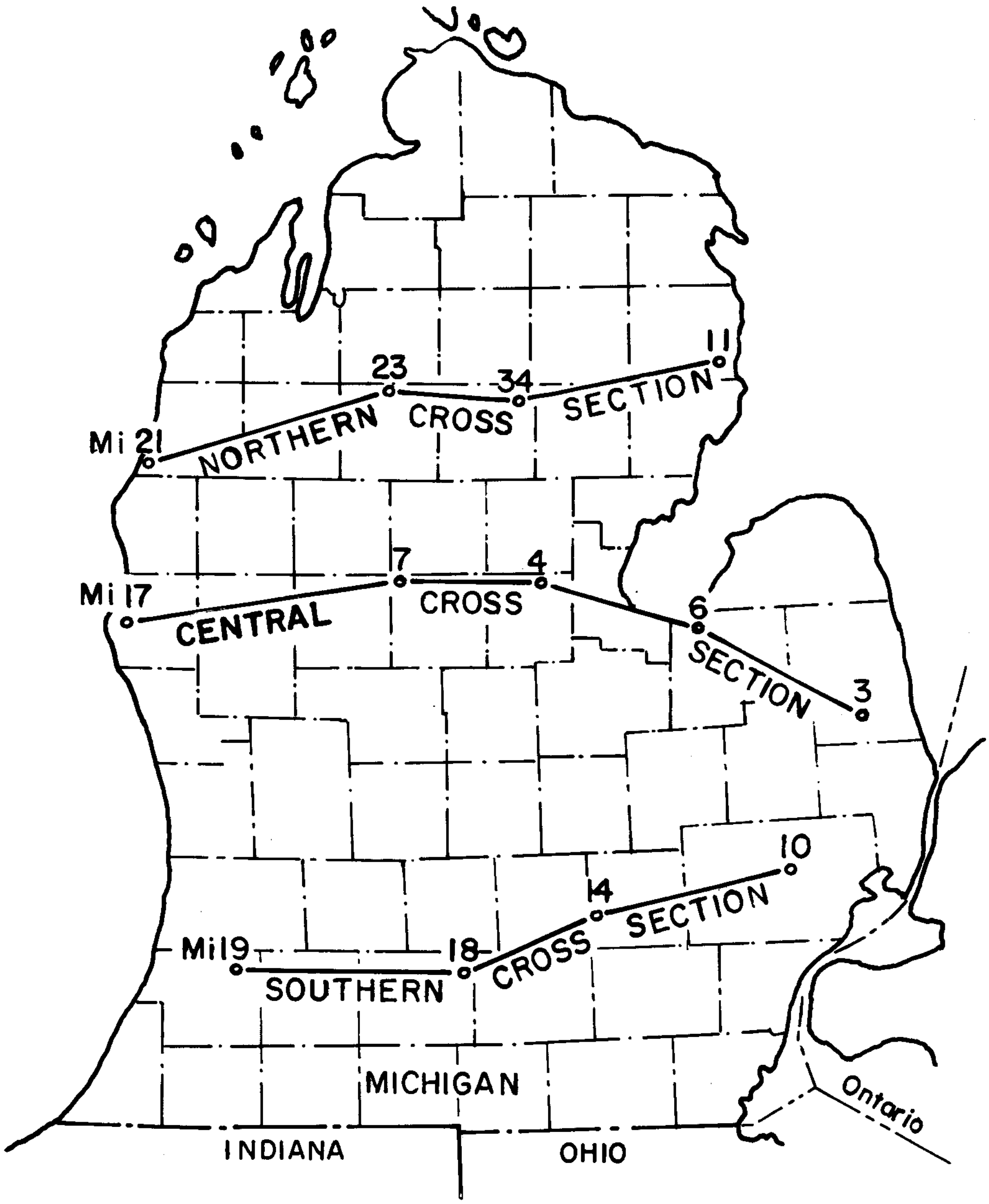

Figure 4. Location of cross-sections.

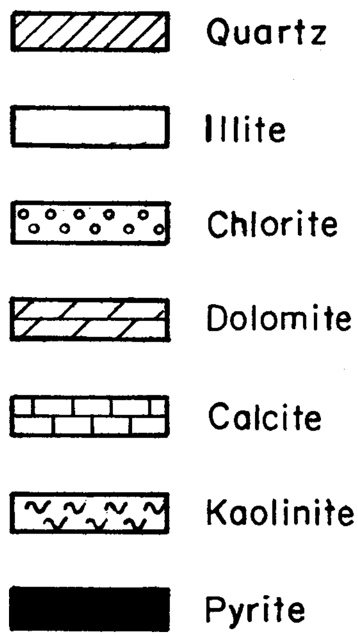

Figure 5. Explanation of symbols on cross-sections (Fig. 6-8).

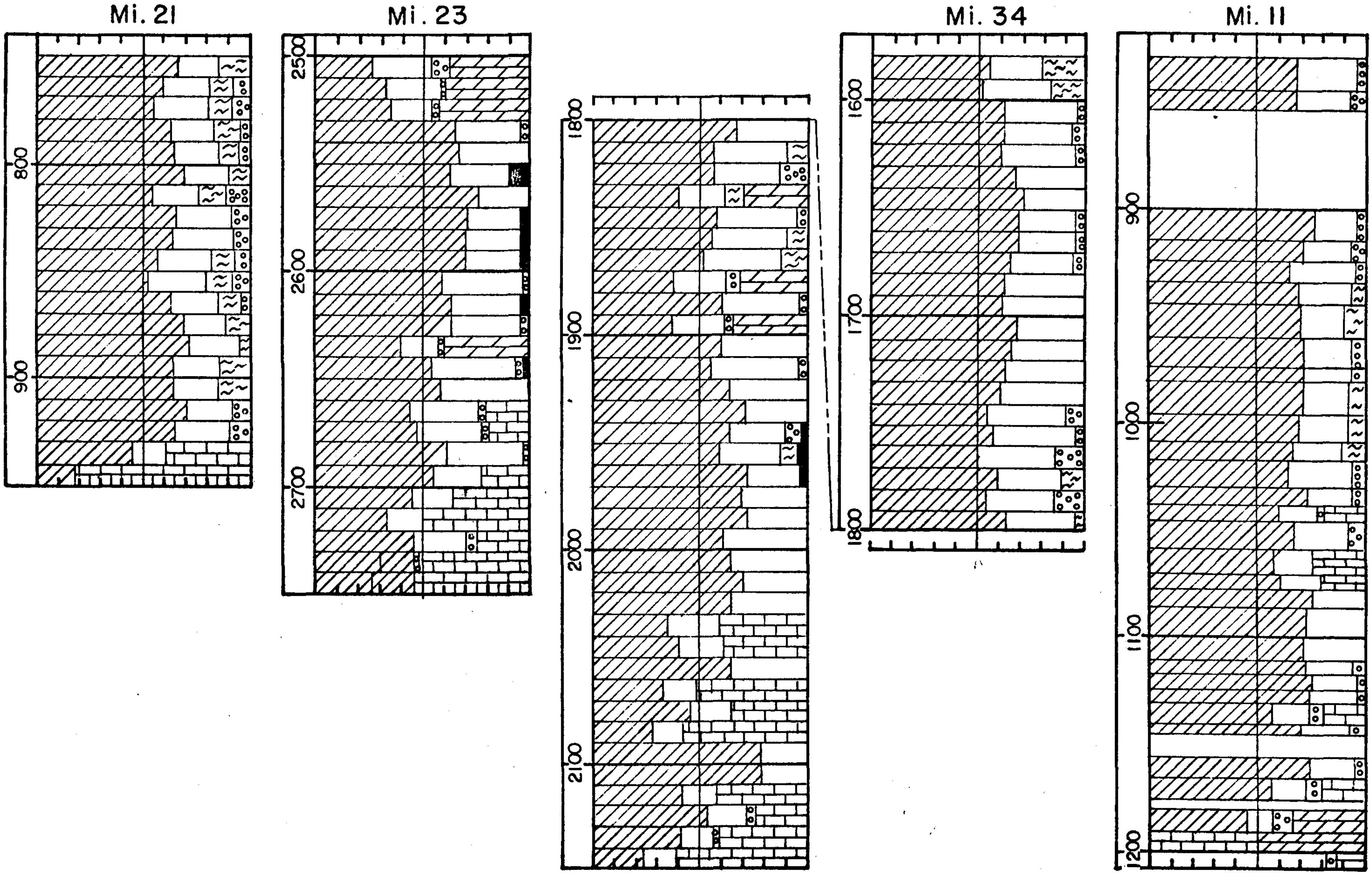

Figure 6. Northern cross-section.

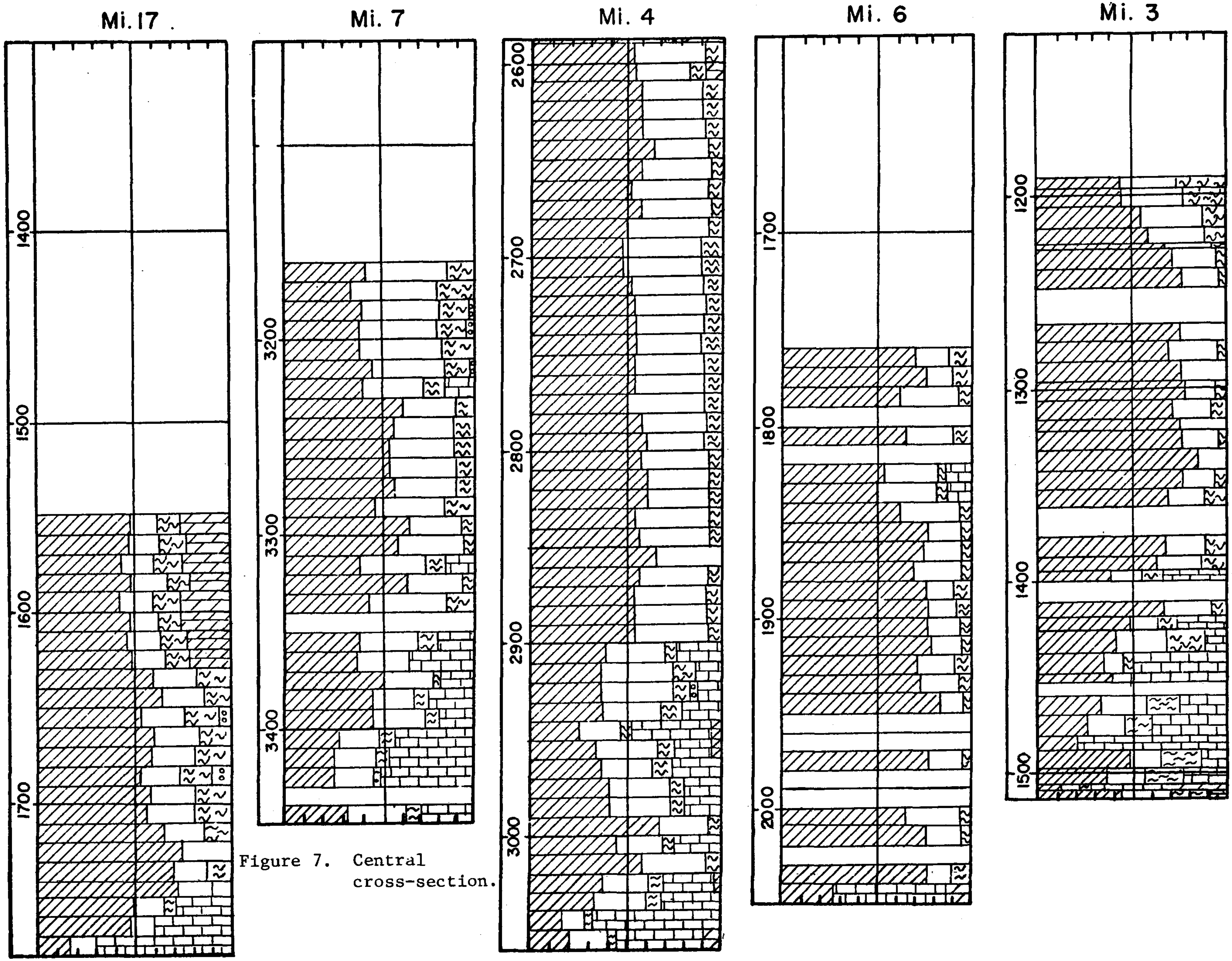

Figure 7. Central cross-section.

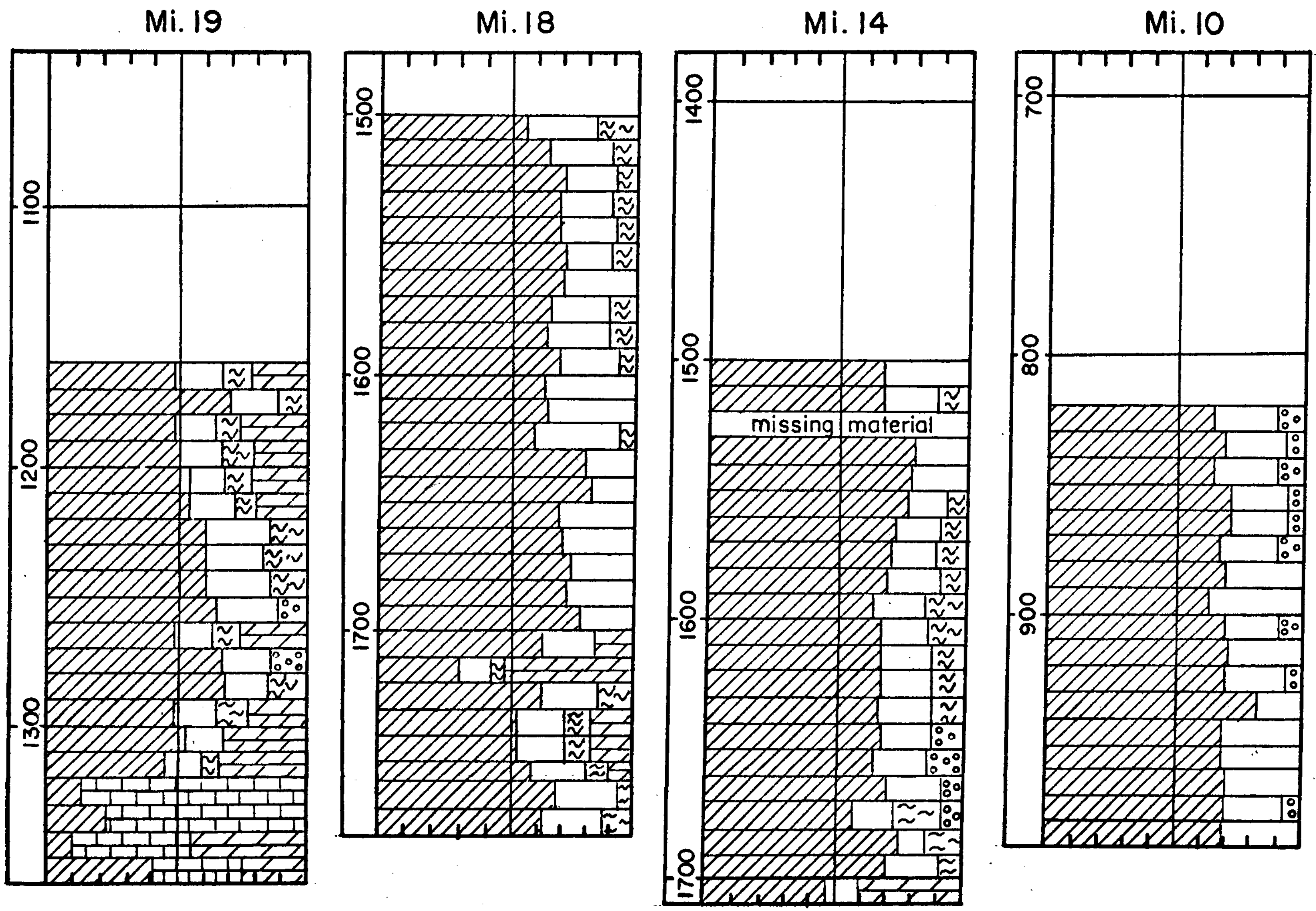

Figure 8. Southern cross-section.

REGIONAL MINERALOGICAL VARIATIONS

Three cross-sections (Fig. 4) have been prepared to illustrate mineralogical variations within the Michigan Basin. These are:

1. The northern cross-section consists of wells MI-21, MI-23, MI-34 and MI-11.

2. The central cross-section consists of wells MI-17, MI-7, MI-4, MI-6, and MI-3.

3. The southern cross-section consists of MI-19, MI-18, MI-14, and MI-10.

The thickest part of the Antrim Shale is encountered approximately at the centers of the northern and central cross-sections, where thicknesses of 500 feet or more are found. Considerable thinning takes place to the west and south, where thicknesses of 100 to 150 feet are found (e.g. well MI-19, Fig. 8).

The base of the Antrim is difficult to distinguish on a purely mineralogical basis, because of the gradational nature of the contact.

Northern Cross-Section

Quartz is the most abundant mineral in all samples of the Antrim Shale except for carbonate rocks in the uppermost part of MI-23 and the lower part of the Antrim.

The most abundant clay mineral is illite, which increases from both east and west margin of the basin toward the center.

Kaolinite is most abundant in the westernmost part of the basin (MI-21, Fig. 6).

Chlorite is found throughout the northern cross-section.

The Antrim Shale in the thickest section of the cross-section (MI-34, Fig. 6) is largely a mixture of quartz and illite.

The dolomite-rich samples of MI-23, 2500-2530 (Fig. 6) are probably Ellsworth Shale.

Central Cross-Section

Quartz is the most abundant mineral in all samples except in carbonate-rich Ellsworth Shale (MI-17, 1550-1630, Fig. 7, for example) and near the base of the Antrim throughout the cross-section. Generally, quartz contents increase from west to east.

Illite is the most abundant clay mineral throughout the wells of the central cross-section. In wells MI-7, MI-6, MI-3, and possibly MI-4, illite contents increase upward in the Antrim Shale.

Kaolinite is clearly more abundant than chlorite throughout the central cross-section.

Southern Cross-Section

Quartz is the most abundant mineral in all samples except for carbonate-rich rocks at the top of MI-19 (Fig. 8) and the base of the Antrim.

Illite is the most abundant clay mineral. Many samples can be described as simple quartz-illite mixtures.

Kaolinite is most abundant in wells MI-19, MI-18, and the upper two-thirds of MI-14.

Chlorite is abundant in the lower portion of MI-14 and MI-10.

CONTENTS OF SELECTED TRACE ELEMENTS

Uranium, thorium, gold, and rare-earth elements were determined by neutron activation at the Phoenix Memorial Laboratory, University of Michigan. All samples were taken from core from well MI-1. Samples 1170 and 12 are from Bedford Shale, 1349.9 and 1352 from a limestone interbed. The results are listed in Appendix B.

Uranium and Thorium

Devonian-Mississippian black shales are known to contain high concentrations of radioactive elements. Beers (1945) first noted high uranium concentrations in the Antrim Shale and its correlation with total carbon content.

Neutron activation and gamma ray spectroscopic results show uranium contents up to 40 ppm (Appendix B), with much lower contents in limestone interbeds. Uranium concentrations show strong positive correlations with pyrite (Fig. 9) and total organic content.

The highest uranium contents tend to be found just beneath thin carbonate interbeds and just beneath the Bedford Shale.

Thorium contents are generally uniform throughout the Antrim, except for much lower contents in limestone interbeds.

Gold

Gold contents range from 0.01 to 0.05 ppm (Appendix B). Concentrations of gold tend to increase downward in the Antrim Shale (Fig. 11).

Rare-Earth Elements

Scandium and hafnium are included among rare-earth elements for the purposes of this paper.

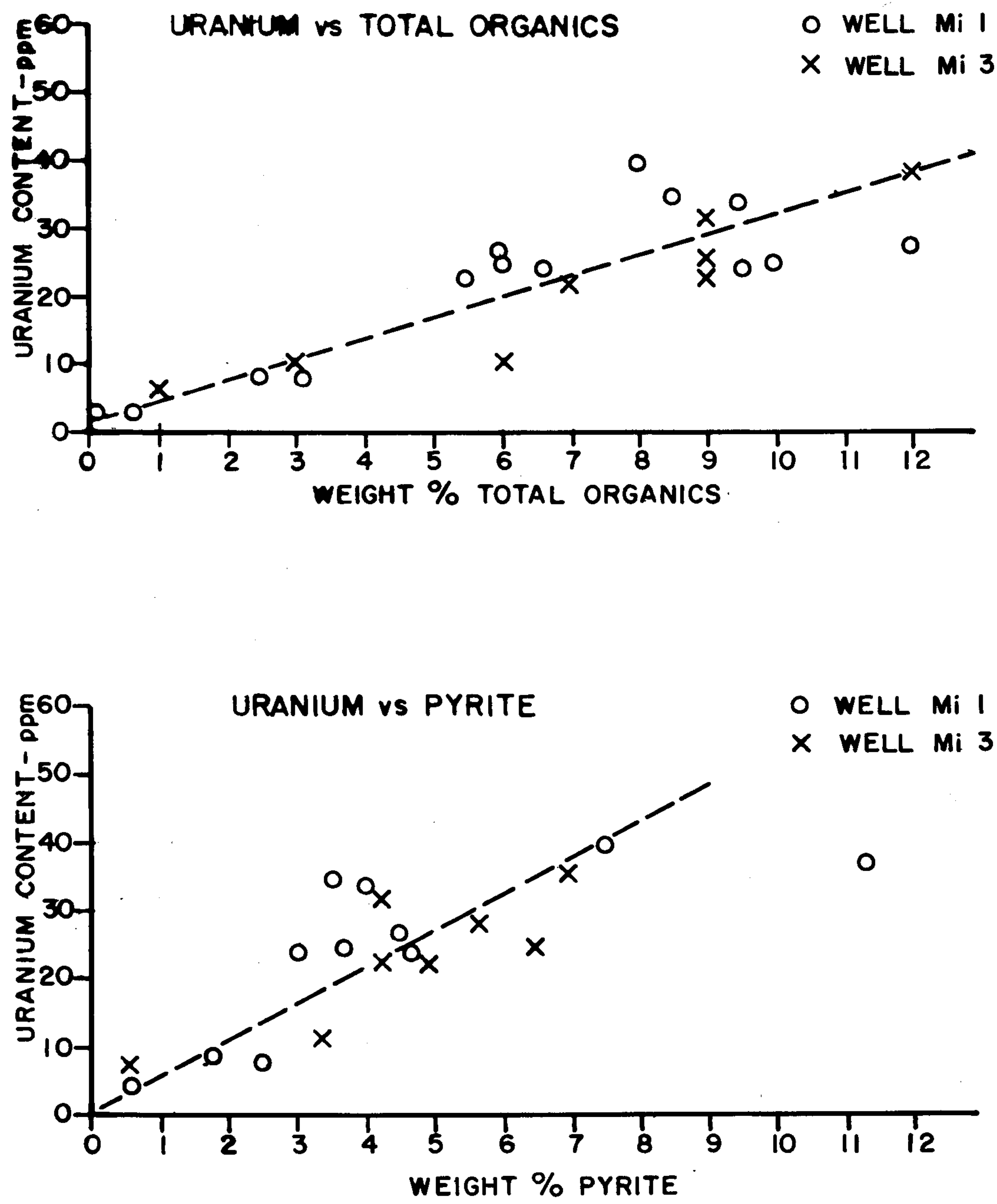

Figure 9. Correlation of uranium with total organic carbon and pyrite.

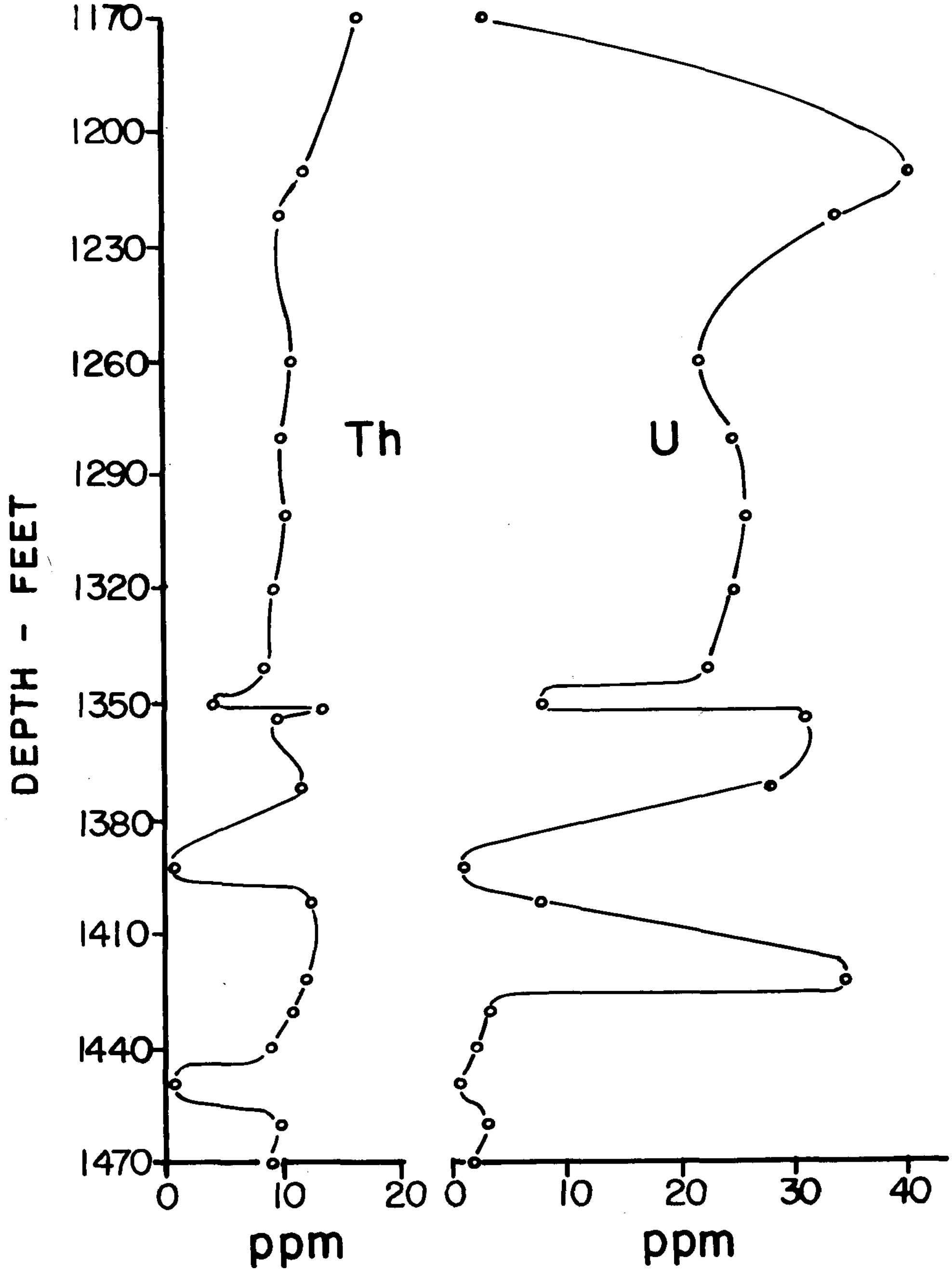

Figure 10. Distribution of uranium and thorium in well MI-1.

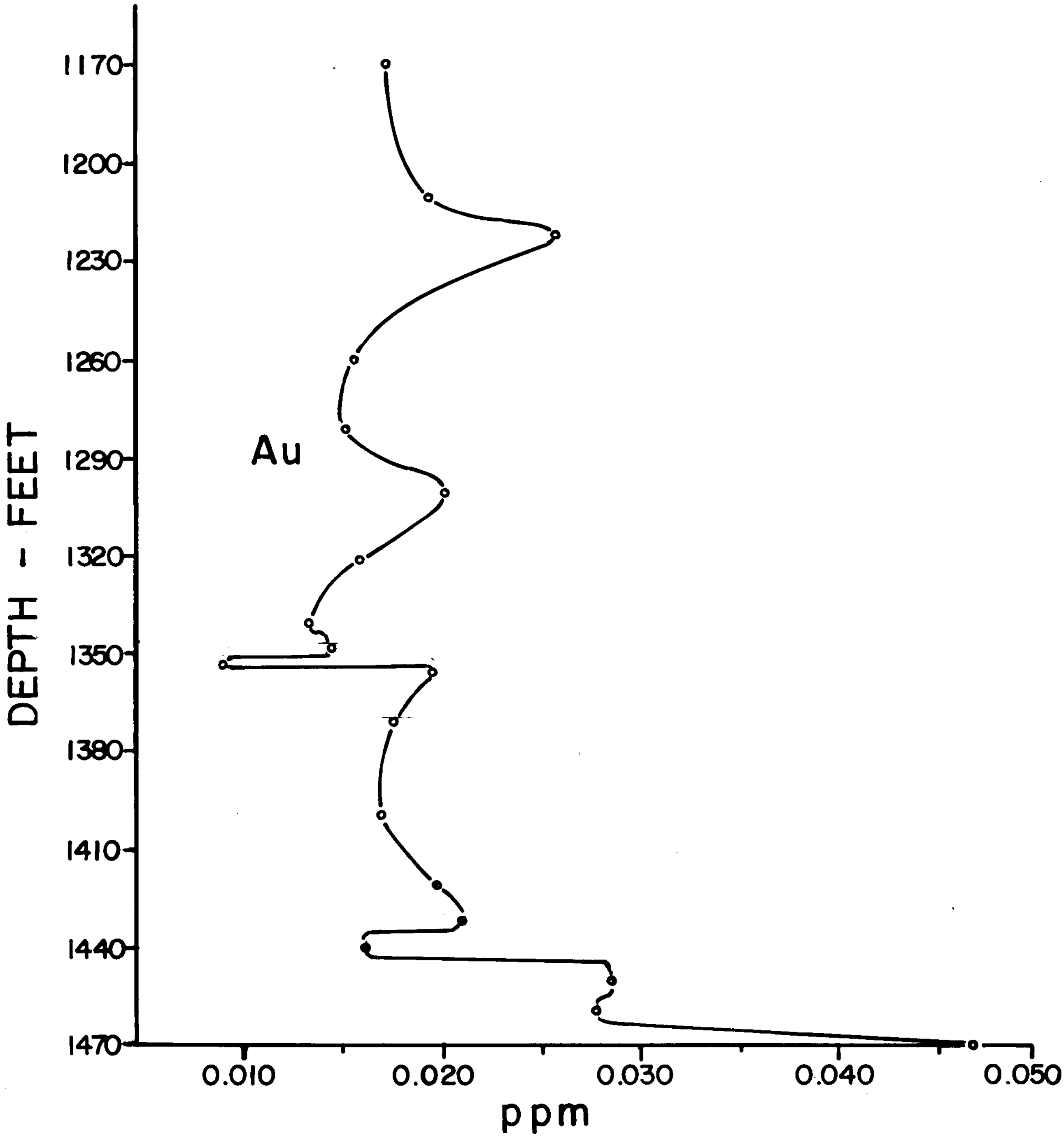

Figure 11. Distribution of gold in well MI-1.

Generally, the contents of rare-earth elements in the Antrim Shale are low. All except lutetium show marked increases upward into Bedford Shale (Figs. 12-15).

CONCLUSIONS

The Antrim Shale differs from Devonian-Mississippian black shales of nearby states in its kaolinite content. Zielinski, et al. (1978) reported only one sample containing kaolinite from Kentucky. Sumartojo and Waldstein (1978) reported no kaolinite from West Virginia and Tennessee, and Harvey, et al. (1978) reported no kaolinite from the New Albany Shale in the Illinoi Basin. Kaolinite in the Antrim Shale, by contrasts ranges to about 10%.

Kaolinite is most abundant in Antrim Shale in two areas:

1. In shallower wells along the eastern margin of the Michigan Basin.

2. In the Ellsworth Shale along the western margin of the Michigan Basin.

The distribution pattern is probably a function of the primary sedimentation pattern in the Michigan Basin, which suggests that the kaolinite along the basin margins represents a proximity to source area.

The illite of the Antrim Shale contains montmorillonite mixed layers. In all cases, except two samples, the mixed layering, if present, appears as asymmetry of the basal illite peak in the X-ray diffraction pattern, suggesting a relatively small percentage of mixed layers. In the other two cases, percentages of mixed layers probably do not exceed 20%. There is no obvious pattern to distribution of mixed layering, neither within individual wells nor in a geographic sense.

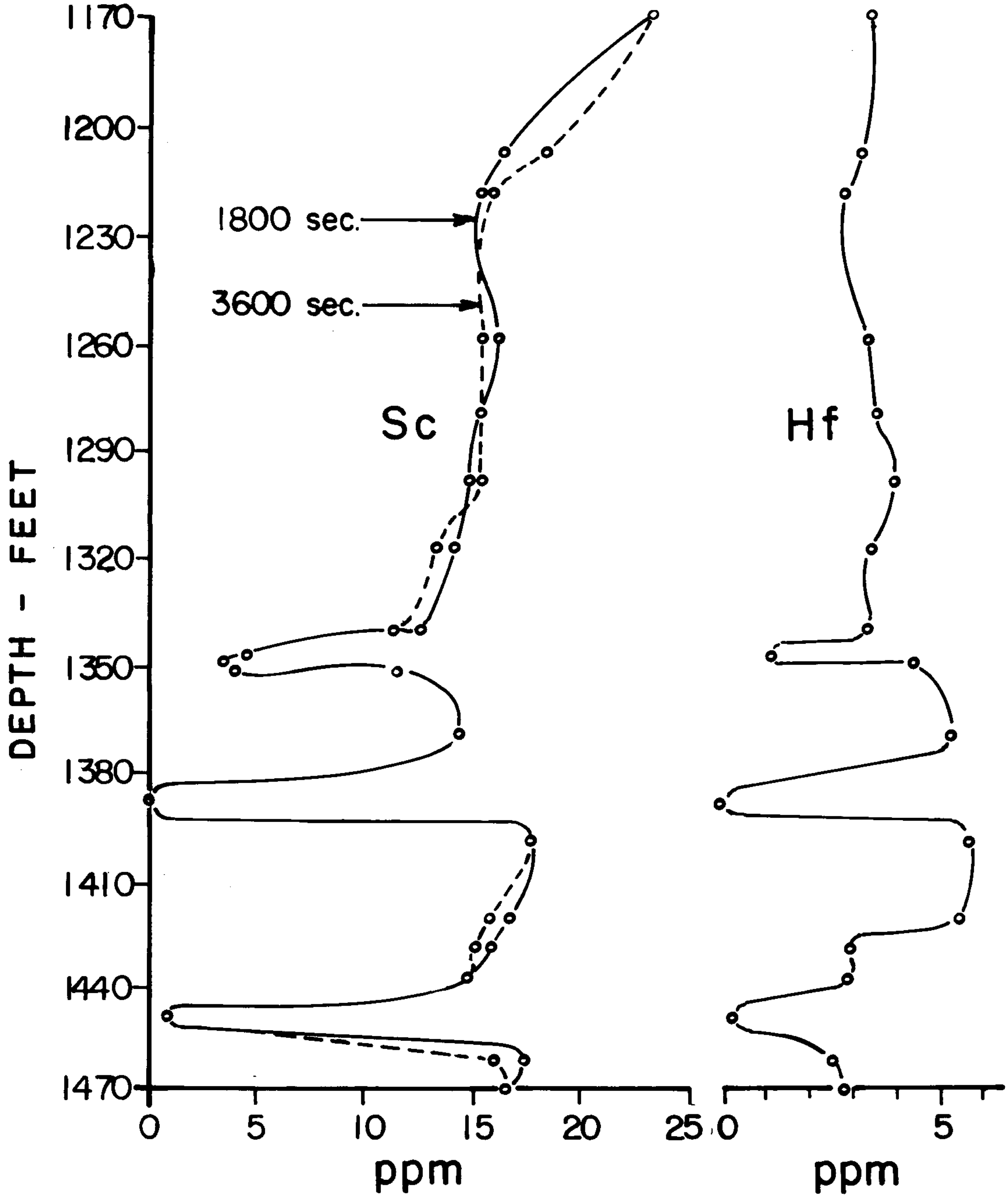

Figure 12. Distribution of scandium and hafnium in well MI-1.

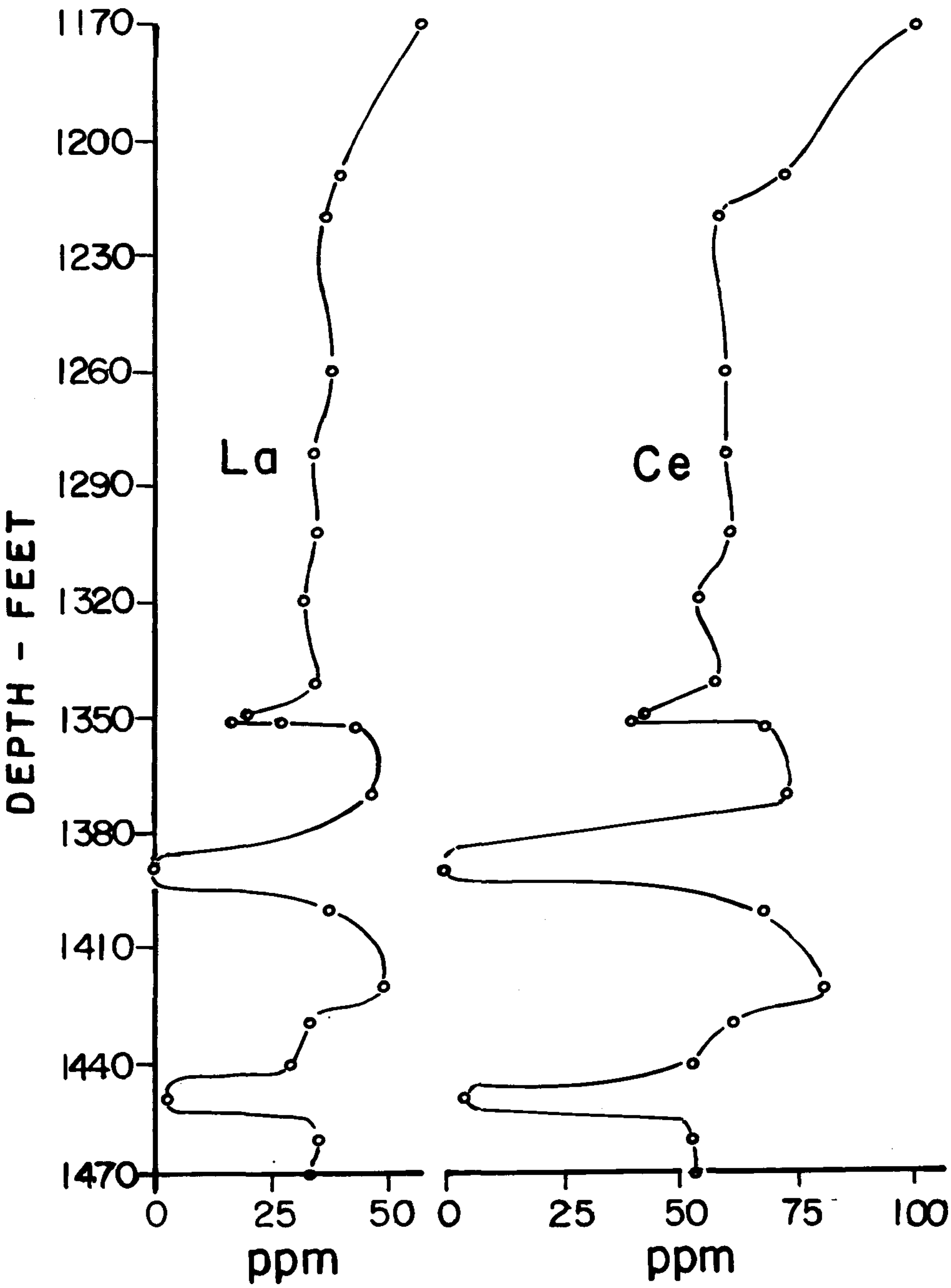

Figure 13. Distribution of lanthanum and cerium in well MI-1.

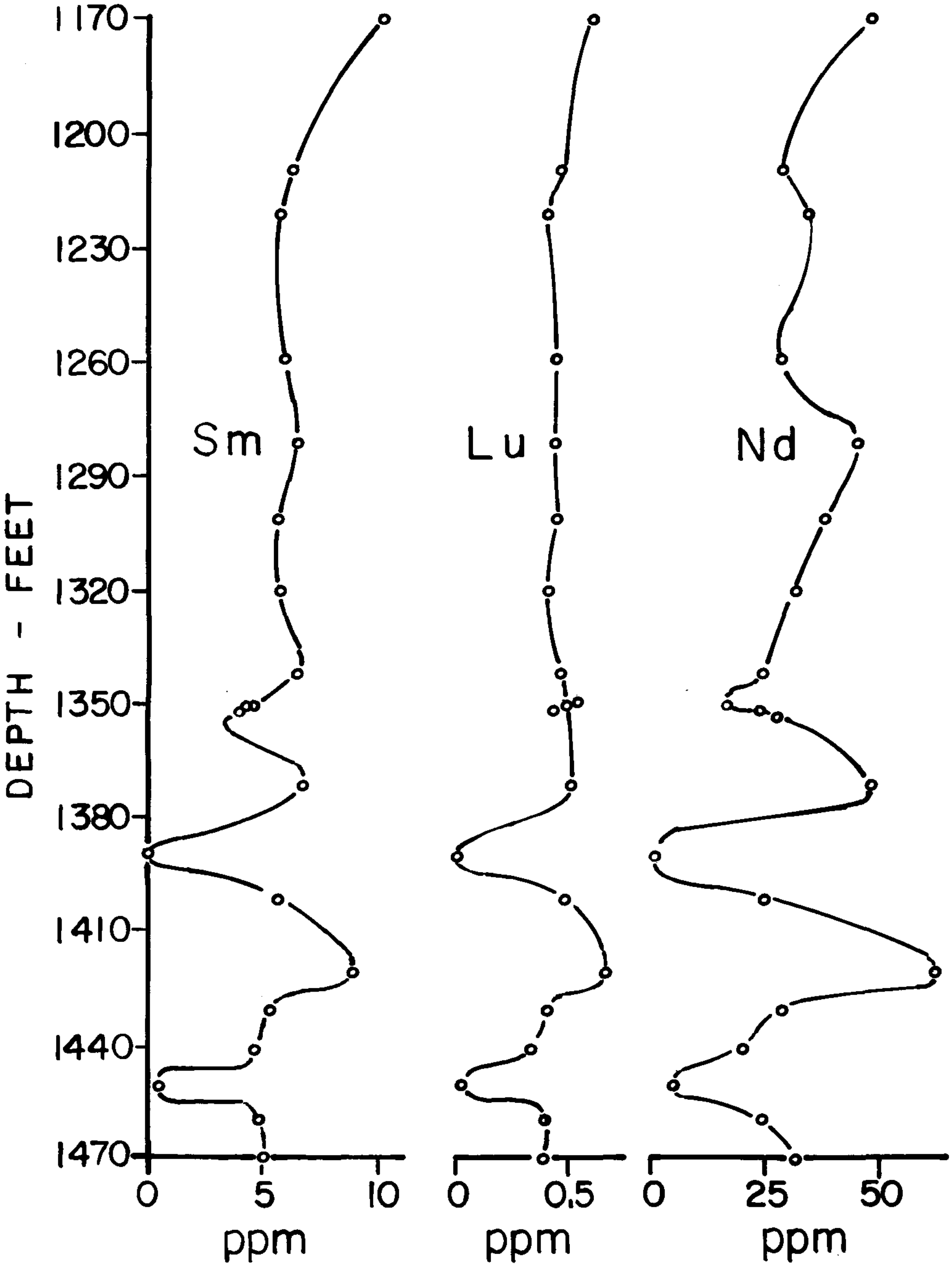

Figure 14. Distribution of samarium, lutetium, and neodynium in well MI-1.

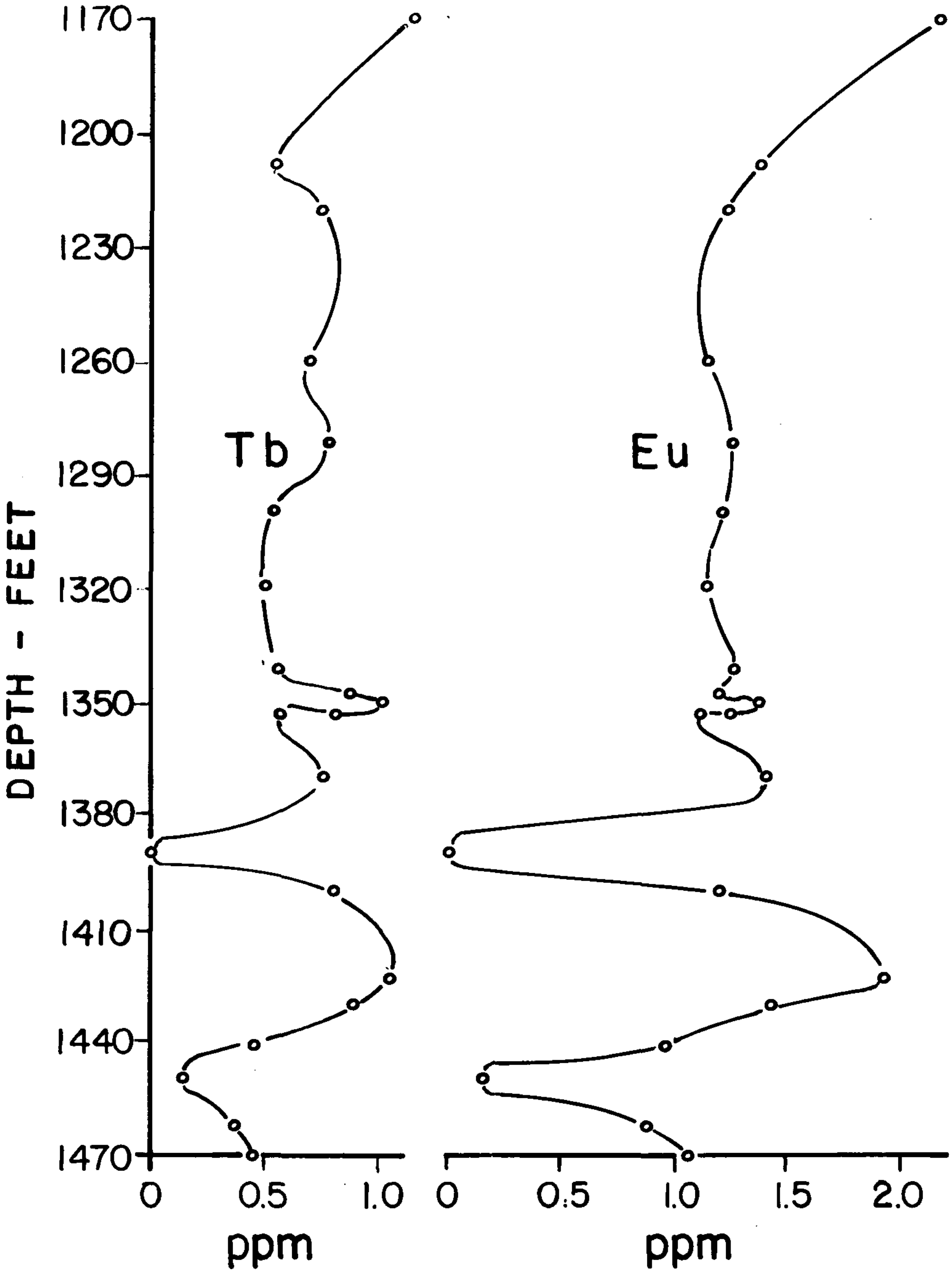

Figure 15. Distribution of terbium and europium in well MI-1.

The Antrim Shale can be distinguished from overlying Bedford Shale on the basis of mineralogy. Bedford Shale contains higher total clays and kaolinite but lower quartz.

Ellsworth Shale, which interfingers with the upper portion of the Antrim, contains much less quartz than Antrim Shale. In addition, Ellsworth Shale contains considerable dolomite.

The contact between Antrim and underlying Traverse Group cannot be determined precisely on the basis of mineralogy. The lower Antrim consists of interbedded shale and limestone and apparently is a transitional contact.

Samples of Antrim Shale that had been retorted at 500°-600°C showed only one phase transformation in which kaolinite became amorphous to X-rays.

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APPENDIX A

Mineral Compositions of Antrim Shale in
Wells MI-1 through MI-26 and MI-34 through MI-36

MI-1

Mineral Components of Core 100

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite
1160.0	42	36	22		
1170.0	43	37	20		
1180.0	39	43	18		
1184.7	45	39	16		
1190.0	37	44	19		
1200.0	37	44	19		
1209.8	52	35	13		
1219.0	69	26	5		
1230.0	62	33	5		
1243.0	70	25	5		
1250.0	63	28	9		
1260.0	57	34	9		
1276.0	49	42	9		
1280.0	68	23	9		
1289.0	70	25	5		
1300.0	70	25	5		
1310.3	70	23	7		
1320.0	68	28	4		
1334.0	68	25	7		
1340.0	68	29	3		
1349.9-1350.7	16				84
1360.0	67	30	3		
1370.4	64	26	10		
1380.4	71	19	10		

MI-1

Mineral Components of Core 100 (Cont'd.)

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite
1392.9	65	25	10		
1400.2	54	33	13		
1410.1	55	31	14		
1420.1	65	25	10		
1429.7	57	28	10		5
1440.6	33	30	10	7	20
1450.6	50				50 (dolomite)
1460.2	20	40	20	7	13
1470.0	32	20	28		20

MI-2

Mineral Components in Core 101

Depth	Quartz	Illite	Kaolinite	Calcite	Dolomite	Pyrite
1150.0	51	28	21			
1160.0	41	38	21			
1170.1	45	30	25			
1180.0	42	38	20			
1188.8	41	37	22			
1199.9	53	26	17			4
1211.2	64	27	7			2
1219.8	71	14	5			
1230.0	72	18	8			2
1241.7	60	31	7			2
1250.0						
1262.0	67	24	7			2
1270.0	60	28	10			2
1279.5	65	33	5			2
1290.5	66	24	8			2
1301.9	74	24				2
1311.1	78	15	5			2
1320.5	75	20	5			2
1325.9	10			80	10	
1330.2	53	26	10			11
1339.8	65	14	8			18
1350.7	60	26	12			2
1360.3	59	28	13			
1369.8	71	21	7			1

MI-2

Mineral Components in Core 101 (Cont'd.)

Depth	Quartz	Illite	Kaolinite	Calcite	Dolomite	Pyrite
1380.1	39	13	5	36	8	
1390.2	72	22	5			1
1400.2	63	26	9			2
1410.0	78	17	4			1
1420.0	50	27	15	8		
1425.8	5			90	5	
1436.6	15			85		
1443.3	27	22	10	41		
1450.0	40	36	17	7		
1459.9	24	22	14	40		
1470.1	53	20	19	8		
1480.3	39	24	22	15		
1490.2	6	6	>5 (∿3)	85		
1500.3	44	22	17	17		
1513.5	14	8	5	73		

MI-3

Antrim Shale - Hole 102

Ratio of Main Constituents in Weight Percent

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1183-1188	43	31	26				
1188-1198	45	32	23				
1198-1208	59	27	13				
1208-1216	60	30	10				
1235-1238	70	20	10				
1238-1248	74	21	5				
1248-1258	81	16	3				
1258-1268	74	24	1				
1268-1278	70	27	3				
1278-1288	77	21	2				
1288-1298	80	14	6				
1298-1308	72	20	8				
1308-1313	78	20	2				
1318-1328	79	18	3				
1328-1338	88	10	2				
1338-1348	77	16	7				
1348-1358	67	21	12				
1368-1378	71	18	11				
1378-1386	64	23	13				
1386-1392	38	19	11		32		
1406-1413	70	22	8				
1413-1420	48	15	11		26		

MI-3

Antrim Shale - Hole 102 (Cont'd.)

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1420-1432	41	25	23		11		
1432-1442	35	11	5		49		
1442-1446	40					60	
1450-1460	33	24	17		25		
1460-1471	27	19	14		40		
1471-1478	20				71	9	
1478-1488	48	17	21		14		
1488-1496	36	21	18		24		
1496-1499	12	10	6		36	35	
1499-1503	44	26	21		9		

MI-4

Antrim Shale - Hole I from Consumers Marsh #1 Cuttings

Detectable Minerals in Ratios of Weight Percent

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
2580-2590	44	26	6			24
2590-2600	56	35	9	tr		
2600-2610	58	34	8	tr		
2610-2620	59	32	9			
2620-2630	58	32	10			
2630-2640	60	32	8			
2640-2650	66	27	7	tr		
2650-2660	61	33	6	tr		
2660-2670	54	39	7	tr		
2670-2680	61	33	6	tr		
2680-2690	54	39	7	tr		
2690-2700	53	39	8			
2700-2710	47	41	12	tr		
2710-2720	48	41	11	tr		
2720-2730	52	39	9			
2730-2740	55	47	8			
2740-2750	56	36	8			
2750-2760	56	35	9			
2770-2780	54	37	9	tr		
2780-2790	57	33	7	tr		
2790-2800	64	27	9			
2800-2810	57	34	7	tr		

MI-4 (Cont'd.)

Antrim Shale - Hole I from Consumers Marsh #1 Cuttings

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
2810-2820	62	28	10	tr		
2820-2830	64	29	7	tr		
2830-2840	55	37	8	tr		
2840-2850	58	35	7	tr		
2850-2860	69	31	tr	tr		
2860-2870	60	34	6			
2870-2880	55	37	8			
2880-2890	55	38	7			
2890-2900	55	39	6			
2900-2910	42	30	6	tr	22	
2910-2920	39	38	10	tr	13	
2920-2930	39	36	8	5	12	
2930-2940	40	30	10	tr	20	
2940-2950	25	22	5		43	5
2950-2960	35	35	10	tr	16	4
2960-2970	37	32	11		20	
2970-2990	44	32	6	tr	18	
2990-3000	68	27	5			
3000-3010	45	23	6		26	
3010-3020	58	34	8			
3020-3030	39	26	8	tr	24	3
3030-3040	34	28	6	tr	32	
3040-3050	17	13	3		67	
3050-3060	21	21	3		45	10

* All depths are in feet, with samples taken over the entire interval indicated.

tr = Mineral is present in detectable amounts less than 3%.

MI-5

Antrim Shale - Hole CC 770 Cuttings

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1170-1180	50	35	15				
1180-1190	58	29	13				
1190-1200	72	22	6				
1200-1210	72	24	4				
1210-1220	missing						
1220-1230	missing						
1230-1240	72	24	4				
1240-1250	72	24	4				
1250-1260	75	20	5		8		
1260-1270	80	18					
1270-1280	73	22	5				
1280-1290	90						
1290-1300	81	13	6				
1300-1310	80	14	6				
1310-1320	77	16	7				
1320-1330	71	22	7				
1330-1340	69	24	9				
1340-1350	60	18	4		18		
1350-1360	30				70		
1360-1370	64	17	7		12		
1370-1380	32	12	6		50		

MI-6

Antrim Shale - Hole I-36

Ratio of Main Constituents in Weight Percent

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1760-1770	70	18	12				
1770-1780	76	13	11				
1780-1790	62	31	7				
1790-1800	90						
1800-1810	65	25	10				
1810-1820	missing						
1820-1830	54	29	3		11		
1830-1840	50	32	5		13		
1840-1850	63	30	7				
1850-1860	78	16	6				
1860-1870	75	20	5				
1870-1880	70	25	5				
1880-1890	76	15	9				
1890-1900	78	14	8				
1900-1910	77	17	6				
1910-1920	79	16	5				
1920-1930	72	22	8				
1930-1940	74	20	6				
1940-1950	85	12	3				
1950-1960	missing						
1960-1970	missing						
1970-1980	78	18	4				
1980-1990	missing						
1990-2000	missing						

MI-6 (Cont'd.)

Antrim Shale - Hole I-36

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2000-2010	67	28	5				
2010-2020	78	18	4				
2020-2030	missing						
2030-2040	78	14	8				
2040-2050	28				58	14	

MI-7

Well MDB2 - 5

Mineral Ratios in Weight Percent

Depth*	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
3160-3170	42	42	14	tr		
3170-3180	37	44	18	tr		
3180-3190	42	40	15	tr		
3190-3200	41	40	16	tr		
3200-3210	41	42	17	tr		
3210-3220	47	38	13	tr		
3220-3230	42	32	11	tr	14	
3230-3240	63	27	9			
3240-3250	57	32	10			
3250-3260	56	33	9	tr		
3260-3270	56	34	9	tr		
3270-3280	58	32	9			
3280-3290	48	37	14	tr		
3290-3300	66	25	7	tr		
3300-3310	60	34	5	tr		
3310-3320	40	34	9	tr	15	
3320-3330	65	28	6	tr		
3330-3340	45	41	13			
3350-3360	39	33	9	tr	18	
3360-3370	38	27	6		29	
3370-3380	56	22	4		14	4
3380-3390	46	27	7		16	4

MI-7 (Cont'd.)

Well MDB2 - 5

Depth*	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
3390-3400	46	29	6	tr	16	3
3400-3410	29	21	8	tr	38	3
3410-3420	26	22	7		44	
3420-3430	25	21	5	tr	42	6
3440-3450	33	30	8	tr	24	4

*All depths are in feet. Samples were taken over the entire interval indicated.

tr = Mineral is present in detectable amounts less than 3%.

** Organic content on determined.

MI-8

Mineral Composition in Weight Percent

Depth*	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1190-1200	37	42	17			
1200-1210	38	38	14			
1210-1220	51	33	8			
1220-1230	50	34	7	tr		
1230-1240	55	30	5	tr		
1240-1250	50	35	7	tr		
1250-1260	50	35	8			
1260-1270	50	39	5	tr		
1270-1280	50	37	5	tr		
1280-1290	56	34	5	tr		
1290-1300	56	34	4	tr		
1300-1310	50	38	5	tr		
1310-1320	55	33	5			
1320-1330	55	34	5	tr		
1330-1340	57	31	5			
1340-1350	67	25	tr			
1350-1360	55	30	6			
1360-1370	49	36	8	tr		
1370-1375	40	29	10	tr	15	

* All depths are in feet. Samples were taken over the entire interval indicated.

tr = Mineral is present in detectable amounts less than 3%.

MI-9

Dow/Erda Kulka Schmidt Rounds Jones No. 1-7

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1840-1850	57	23	19			
1850-1860	59	23	18			
1860-1870	63	21	16			
1870-1880	68	21	11			
1880-1890	69	19	12			
1890-1900	77	15		8		
1900-1910	62	26		12		
1910-1920	68	27		5		
1920-1930	68	24		8	tr	
1930-1940	70	24		6	tr	
1940-1950	66	24		10		
1950-1960	65	26		9		
1960-1970	67	23		10		
1970-1980	68	32				
1980-1990						
1990-2000	69	31		tr	tr	
2000-2010	71	24		5		
2010-2020	70	23		7		
2020-2030	71	23		6		
2030-2040	68	26		4		
2040-2050	61	39				
2050-2060	70	23		7		
2060-2070	70	23		7		
2070-2080	61	15	25		tr	tr

MI-10

Reef Petroleum Smitha 4-1

Depth	Quartz	Illite	Chlorite
820-830	65	25	10
830-840	70	24	6
840-850	65	26	9
850-860	72	22	6
860-870	72	22	6
870-880	68	24	8
880-890	70	30	
890-900	64	36	
900-910	70	22	8
910-920	72	28	
920-930	71	23	6
930-940	83	17	
940-950	69	31	
950-960	69	33	
960-970	70	30	
970-980	70	23	7
980-990	69	31	

MI-11

Elek-Bartlett Schrade #1

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
830-840	68	29		3		
845-855	68	23		7		
Missing interval						
900-915	76	20		4		
915-924	71	22		7		
924-934	64	32		4		
934-944	68	25	7			
944-960	69	21	10			
960-973	70	23		7		
973-980	70	23		7		
985-996	71	21	8			
996-1008	69	23	8			
1008-1017	66	24	12			
1017-1029	63	30		7		
1029-1038	72	21		7		
1038-1046	59	18		3	20	
1046-1058	66	26		8		
1058-1070	57	15		3	25	
1070-1077	59	19			22	
1077-1086	74	26				
1086-1100	71	29				
1100-1110	70	30				
1110-1117	71	22		7		

MI-11 (Cont'd.)

Elek-Bartlett Schrade #1

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1117-1124	74	22		4		
1124-1130	73	23		4		
1130-1140	55	18		7	20	
1140-1145	69	23		8		
1156-1165	73	21		6		
1165-1171	56	17		6	21	
1180-1190	44	12		9	35	
1190-1197	5				55	45
1197-1200					40	60
1200-1207	59	21		5	15	

MI-12

Bauchem K-6

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1320-1330	70	18	12			
1330-1340	65	17	13			
1340-1350	64	21	15			
1350-1360	70	30				
1360-1370	71	11	18			
1370-1380	73	27				
1380-1390	72	21	7			
1390-1400	73	22		5		
1400-1410	72	28				
1410-1420	73	27				
1420-1430	69	22		9		
1430-1440	66	24		10		
1440-1450	67	33				
1450-1460	63	37				
1460-1470	73	27				
1470-1480						
1480-1490	64	36				
1490-1500	70	30				
1500-1510	69	31				
1510-1520	66	34				
1520-1530	58	18				25
1530-1540	67	23		10		

MI-12

Bauchem K-6

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1540-1550	61	17				
1550-1560	64	36		9		22
1560-1570	70	21		9		
1570-1580	79	21				
1580-1590	63	27				
1590-1600	75	25				
1600-1610	75	25				
1610-1620	75	25				
1620-1630	70	36				
1630-1640	55	45				
1640-1650	77	23				
1650-1660	57	15			28	
1660-1670	74	21		5		
1670-1680	54	19			27	
1680-1690	51	13			36	
1690-1700	72	28				
1700-1710	80	20				
1710-1720	66	12			22	
1720-1730	51	11			38	
1730-1740	73	27				

MI-13

Hunt Energy/Wild

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2610-2620	55	33	12				
2620-2630	46	38	16				
2630-2640	33	17				50	
2640-2650	70	21	9				
2650-2660	81	19					
2660-2670	80	20					
2670-2680	63	28	9				
2680-2690	69	31					
2690-2700	64	28	8				
2700-2710	67	24	9				
2710-2720	66	27	7				
2720-2730	68	26	6				
2730-2740	70	23	7				
2740-2750	72	28					
2750-2760	68	32					
2760-2770	75	25					
2770-2780	61	33	6				
2780-2790	70	24	6				
2790-2800	61	29	10				
2800-2810	56	35	9				
2810-2820	55	33	12				
2820-2830	61	29	10				
2830-2840	61	29	10				
2840-2850	56	34	10				
2850-2860	54	32	14				

MI-13 (Cont'd.)

Hunt Energy/Wild

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2860-2870	57	32	11				
2870-2880	70	30					
2880-2890	63	29		8			
2890-2900	53	34	13				
2900-2910	61	35		4			
2910-2920	71	25		4			
2920-2930	57	29	4				
2930-2940	58	30	12				
2940-2950	62	29	9				
2950-2960	63	33	4				
2960-2970	60	35	5				
2970-2980	61	30	9				
2980-2990	60	30	6				4
2990-3000	59	31	4				6
3000-3010	69	25					6
3010-3020	70	26					4
3020-3030	71	21					8
3030-3040	67	25					8
3040-3050	70	23					7
3050-3060	70	26					4
3060-3070	61	35					4
3070-3080	63	32					5
3080-3090	62	27		6			5
3090-4000	43	31		2	24		

Amoco Production Patrick 1-28

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1490-1500						
1500-1510	68	32	tr			
1510-1520	68	21	11			
1520-1530						
1530-1540	80	20				
1540-1550	79	21				
1550-1560	78	15	7			
1560-1570	73	17	10			
1570-1580	71	17	12			
1580-1590	70	21	9			
1590-1600	64	21	15			
1600-1610	68	18	14			
1610-1620	68	20	12			
1620-1630	68	20	12			
1630-1640	67	21	12			
1640-1650	68	19		13		
1650-1660	65	21		14		
1660-1670	70	21		9		
1670-1680	57	23	18	9		
1680-1690	65	20	15			
1690-1700	70	20	10			
1700-1710	47	12				41

MI-15

Hunt Energy Weber 1-26

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1070-1080	72	21	7			
1080-1090	65	20	15			
1090-1100	70	30				
1100-1110	70	20	10			
1110-1120	76	24	tr	tr		
1120-1130	75	17	8			
1130-1140	70	20	10			
1140-1150	70	19	11			
1150-1160	70	19	11			
1160-1170	70	18	12			
1170-1180	66	20	14			
1180-1190	63	21	16			
1190-1200	68	17	15			

MI-16

Well MI-16 Amoco Fawcett 3-24

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1760-1770	59	24	12	5		tr
1770-1780	40	20	14	6		20
1780-1790	46	17	9	5		23
1790-1800	48	17	11			24
1800-1810	46	18	11			25
1810-1820	70	18	12			
1820-1830	64	21	15			
1830-1840	70	19		11		
1840-1850	65	21		14		
1850-1860	65	21		14		
1860-1870	62	22		16		
1870-1880	65	21		14		
1880-1890	68	32	tr	tr		
1890-1900	63	23	14			
1900-1910	63	20	17		tr	
1910-1920	49	18	15		18	
1920-1930	50	16	9			25
1930-1940	70	30	tr	tr		
1940-1950	74	36	tr	tr		
1950-1960	73	27	tr	tr	tr	
1960-1970	66	20	14		tr	

MI-16 (Cont'd.)

Well MI-16 Amoco Fawcett 3-24

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1970-1980	65	21	14		tr	
1980-1990	60	20	20			
1990-2000	55	23	22			
2000-2010	63	20	16		tr	tr
2010-2020	65	35	tr	tr		
2020-2030	54	22	23			

MI-17

Well MI-17 Amoco Tompkins 1-2

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
1550-1560	49	14	12			25
1560-1570	48	16	14			22
1570-1580	44	18	14			24
1580-1590	49	19	11			21
1590-1600	43	18	15			24
1600-1610	48	15	13			24
1610-1620	47	17	14			22
1620-1630	49	18	12			21
1630-1640	60	23	17			tr
1640-1650	65	22	13			
1650-1660	53	23	18	6		
1660-1670	61	23	16			
1670-1680	59	23	18			
1680-1690	52	21	17	10		
1690-1700	58	24	18			
1700-1710	56	25	19			
1710-1720	65	21	14			
1720-1730	74	26				tr
1730-1740	70	17	13		tr	tr
1740-1750	73	18	9			
1750-1760	50	15	6		28	
1760-1770	48	12			40	
1770-1780	17	14			69	tr

MI-18

Don Scott - Collier 1-12

Depth	Quartz	Illite	Kaolinite	Dolomite
1500-1510	59	26	15	
1510-1520	68	24	8	
1520-1530	74	19	7	
1530-1540	72	20	8	
1540-1550	72	21	7	
1550-1560	74	18	8	
1560-1570	73	27		
1570-1580	68	23	9	
1580-1590	66	25	9	
1590-1600	71	23	6	
1600-1610	65	23	12	
1610-1620	66	34		
1620-1630	62	32		
1630-1640	82	18		
1640-1650	84	16		
1650-1660	71	29		
1660-1670	72	28		
1670-1680	76	24		
1680-1690	74	19	7	
1690-1700	79	21		
1700-1710	64	20		16

MI-18 (Cont'd.)

Don Scott - Collier 1-12

Depth	Quartz	Illite	Kaolinite	Dolomite
1710-1720	33	11	5	51
1720-1730	64	23	13	
1730-1740	55	19	9	17
1740-1750	55	19	9	17
1750-1760	61	21	8	10
1760-1770	70	24	6	
1770-1780	64	24	12	

MI-19

Well MI-19 Kulka & Schmidt-Guldemond 1-21

Depth	Quartz	Illite	Kaolinite	Chlorite	Illite	Dolomite
1160-1170	51	18	11			20
1170-1180	72	18	10			tr
1180-1190	50	16	9			25
1190-1200	52	16	13			19
1200-1210	56	13	11			20
1210-1220	56	17	8			19
1220-1230	62	25	13			tr
1230-1240	62	22	16			tr
1240-1250	62	24	14			tr
1250-1260	66	23		11		tr
1260-1270	50	14	11			25
1270-1280	68	19		13		tr
1280-1290	69	17	14			tr
1290-1300	49	17	12			22
1300-1310	54	14				32
1310-1320	46	14	7			33
1320-1330	14	tr	tr		86	tr
1330-1340	23	tr	tr		77	tr
1340-1350	10	3	2		35	49
1350-1360	41	10	8		16	25

MI-20

Crystal Exploration - Ulrich #1

Depth	Quartz	Illite	Kaolinite	Dolomite
1770-1780	68	25	7	
1780-1790	68	17	15	
1790-1800	68	18	14	
1800-1810	68	18	14	
1810-1820	79	19	2	
1820-1830	79	21		
1830-1840	75	19	6	
1840-1850	72	25	3	
1850-1860	70	30		
1860-1870	78	18	4	
1870-1880	78	18	4	
1880-1890	37	12		51
1890-1900	71	23	6	
1900-1910	72	28		
1910-1920	70	30		
1920-1930	74	18	8	
1930-1940	68	27	5	
1940-1950	35	19	3	43
1950-1960	70	24	6	
1960-1970	56	44		
1970-1980	45	7	3	45

MI-21

Aztec State Unit 3-2

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite
750-760	65	19	16		1	tr
760-770	58	23	10	9		tr
770-780	54	26	10	10		tr
780-790	62	21	11	6		
790-800	64	20	9	7		
800-810	68	18	10	tr		
810-820	53	25	13	12		
820-830	65	25		10		
830-840	63	28		9		
840-850	56	26	10	8		
850-860	52	27	12	9		
860-870	62	23	10	5		
870-880	68	20	12	tr		
880-890	71	23	6			
890-900	63	22	15			
900-910	63	21	16			
910-920	70	21		9		
920-930	64	26		10		
930-940	44	12	tr	tr	40	
940-950	10	8			82	

MI-22

American Tech. Explor.-Dart. Wiser-Broderick 1-9

Depth	Quartz	Illite	Kaolinite	Calcite	Dolomite
1820-1830	65	26	9		
1830-1840	69	31			
1840-1850	74	26			
1850-1860	72	28			
1860-1870	71	29			
1870-1880	71	22	7		
1880-1890	63	37			
1890-1900	68	24	8		
1900-1910	76	24			
1910-1920	74	22	4		
1920-1930	71	29			
1930-1940	73	21	6		
1940-1950	73	27			
1950-1960	71	29			
1960-1970	71	29			
1970-1980	44	12			44
1980-1990	43	14			43
1990-2000	70	30			trace
2000-2010	72	28			
2010-2020	77	23			
2020-2030	79	21			
2030-2040	74	26			
2040-2050	71	23	6		
2050-2060	76	19	5		

MI-22 (Cont'd.)

American Tech. Explor.-Dart. Wiser-Broderick 1-9

Depth	Quartz	Illite	Kaolinite	Calcite	Dolomite
2060-2070	74	26			
2070-2080	76	24			
2080-2090	73	27			
2090-2000	67	33			
2100-2110	68	25	7		
2110-2120	74	26			
2020-2030	80	20			
2030-2040	81	19			
2040-2050	78	22			
2050-2060	43	14		43	
2060-2070	12	2			86

MI-23

Dart B & L Unit

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2500-2510	27	27		9		43	
2510-2520	33	26		2		39	
2520-2530	35	20		3		42	
2530-2540	65	31		4			
2540-2550	67	33					
2550-2560	63	27					10
2560-2570	76	24					
2570-2580	71	24					5
2580-2590	70	25					5
2590-2600	70	25					5
2600-2610	58	39		3			
2610-2620	63	33					4
2620-2630	63	33		4			
2630-2640	39	28		3		30	
2640-2650	53	40		3			4
2650-2660	57	43					
2660-2670	43	32		3	22		
2670-2680	47	30		3	20		
2680-2690	60	37		3			
2690-2700	54	23			23		
2700-2710	44	19			37		
2710-2720	32	17			51		
2720-2730	45	24		5	26		
2730-2740	29	16		2	53		
2740-2750	25	20			55		

MI-24

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1080-1090	75	22		6			
1090-1100	72	22	3	3			
1100-1110	65	23	12				
1110-1120	68	27	5				
1120-1130	65	25	10				
1130-1140	63	25	12				
1140-1150	63	24	8	5			
1150-1160	70	25		5			
1160-1170	65	32	3				
1170-1180	67	33	tr	tr	tr	tr	
1180-1190	70	27		3			
1190-1200	67	29		4			
1200-1210	69	28		3			
1210-1220	63	37					
1220-1230	65	31		4			
1230-1240	23	8			69		

MI-25

Mineral Percentages

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2040-2050	36	24		8		32	
2050-2060	42	27		7		24	
2060-2070	40	24		6		30	
2070-2080	39	28		7		26	
2080-2090	34	28		7		31	
2090-3000	38	26		7		29	
3000-3010	32	28		8		32	
3010-3020	34	29		6		27	4
3020-3030	37	18		2		38	5
3030-3040	41	17		2		35	5
3040-3050	41	24		8		22	5
3050-3060	64	31					5
3060-3070	61	27		7			5
3070-3080	61	30		3			6
3080-3090	56	31		4			10
3090-3100	58	36		3			5
3100-3110	43	24	3		30		
3110-3120	40	27	4		24		5
3120-3130	45	36	5	3	11		
3130-3140	39	24		2	35		
3140-3150	39	26		3	32		
3150-3160	32	21		2	40		5

MI-25 (Cont'd.)

Mineral Percentages

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
3160-3170	52	17			26		5
3170-3180	51	19			25		5
3180-3190	45	21	7		27		
3190-3200	48	22	6		24		
3200-3210	29	17		tr	54		
3210-3220	25	21		4	50		

MI-26

Mineral Percentages

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1200-1210	44	23	8		25		
1210-1220	47					53	
1220-1230	45					55	
1230-1240	61	34	5				
1240-1250	31	25	8			41	
1250-1260	62	32		6			
1260-1270	52	46		2			
1270-1280	68	32					
1280-2190	64	29	7				
1290-1300	62	38					
1300-1310	66	29		5			
1310-1320	66	34					
1320-1330	55	34	11				
1330-1340	61	30	9				
1340-1350	59	38		3			
1350-1360	62	34		4			
1360-1370	31	16		3	50		
1370-1380	25	18		2	13		
1380-1390	61	34		5			
1390-1400	59	37		4			
1400-1410	47	21		4	28		
1410-1420	41	23		3	33		
1420-1430	31	14		4	36	16	

MI-34

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1580-1590	56	24	20				
1590-1600	53	32	15				
1600-1610	63	35		2			
1610-1620	63	32		5			
1620-1630	61	35		4			
1630-1640	68	32					
1640-1650	73	27					
1650-1660	70	26		4			
1660-1670	70	26		4			
1670-1680	65	30		5			
1680-1690	63	37					
1690-1700	62	38					
1700-1710	68	32					
1710-1720	66	34					
1720-1730	63	37					
1730-1740	61	39					
1740-1750	55	37		8			
1750-1760	58	38		4			
1760-1770	52	35		13			
1770-1780	60	30	10				
1780-1790	54	32		24			
1790-1800	64	32	4				
1800-1810	67	33					
1810-1820	56	34	10				

MI-34 (Cont'd.)

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
1820-1830	56	31		13			
1830-1840	40	21	9			30	
1840-1850	58	37		5			
1850-1860	55	35	10				
1860-1870	51	36	13				
1870-1880	37	25		7		32	
1880-1890	60	36		4			
1890-1900	36	25		3		36	
1900-1910	59	41					
1910-1920	54	41		5			
1920-1930	63	37					
1930-1940	70	30					
1940-1950	63	26		8			3
1950-1960	58	29	8				5
1960-1970	71	25					4
1970-1980	69	31					
1980-1990	72	28					
1990-2000	60	40					
2000-2010	63	37					
2010-2020	69	31					
2020-2030	63	37					
2030-2040	34	25			41		
2040-2050	40	20			40		
2050-2060	63	37					
2060-2070	32	15			53		

MI-34 (Cont'd.)

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2070-2080	45	19			36		
2080-2090	27	14			59		
2090-2100	78	22					
2100-2110	78	22					
2110-2120	42	16			42		
2120-2130	53	19		4	24		
2130-2140	41	16		2	41		
2140-2150	23	16			61		

MI-35

Mineral Percentages

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
550-560	43	20		3		34	
560-570	42	24	2	3		29	
570-580	35	19	5			41	
580-590	40	23	3			34	
590-600	44	21		3		32	
600-610	40	16	4			40	
610-620	65	32		3			
620-630	70	30					
630-640	61	31	8				
640-650	59	35	6				
650-660	68	23	9				
660-670	94	4	2				
670-680	70	25					5
680-690	20				45	35	

MI-36

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2090-2100	56	27		3		14	
2100-2110	46	28		3		13	
2110-2120	65	28	7				
2120-2130	64	31		5			
2130-2140	68	29		3			
2140-2150	68	27		5			
2150-2160	64	29	7				
2160-2170	60	32	8				
2170-2180	65	32		3			
2180-2190	55	35	10				
2190-2200	57	38		5			
2200-2210	54	37	9				
2210-2220	58	38		4			
2220-2230							
2230-2240							
2240-2250	58	33	9				
2250-2260	55	35	10				
2260-2270	63	30	7				
2270-2280	57	35	8				
2280-2290	67	33					
2290-2300	65	32		3			
2300-2310	61	35		4			
2310-2320	58	35	7				
2320-2330	63	30	7				
2330-2340	63	37					

MI-36 (Cont'd.)

Depth	Quartz	Illite	Kaolinite	Chlorite	Calcite	Dolomite	Pyrite
2340-2350	52	38	10				
2350-2360	60	37		3			
2360-2370	65	31		4			
2370-2380	63	33		4			

APPENDIX B

Concentration of Selected Trace Elements
in Well MI-1

NEUTRON ACTIVATION ANALYSIS CONCENTRATIONS OF TRACE ELEMENTS, MI-1

Depth	Ce	Tb	Eu	Sm	Lu	Nd	La	Sc	Hf	Th	U	Au
1170.0	102.6	1.13	2.19	10.5	0.62	49.48	59.5	23.5	3.59	17.12	3.99	0.0167
1210.0	74.2	0.54	1.39	6.5	0.50	35.56	41.8	16.9	3.32	12.13	40.05	0.0193
1220.0	61.9	0.73	1.25	5.9	0.45	35.3	38.3	15.6	2.91	10.47	34.29	0.0258
1260.0	62.9	0.69	1.15	6.1	0.45	29.3	39.2	16.3	3.36	11.23	22.26	0.0157
1280.0	62.3	0.78	1.25	6.4	0.43	46.8	36.6	15.5	3.57	10.53	24.90	0.0151
1300.0	63.3	0.55	1.21	6.0	0.47	39.4	35.6	15.2	4.00	10.56	26.55	0.0204
1320.0	56.2	0.52	1.16	5.9	0.40	32.5	33.9	14.06	3.49	9.97	23.83	0.0159
1340.0	58.3	0.54	1.23	6.5	0.47	25.6	35.6	12.56	3.04	9.47	22.90	0.0133
1349.9	38.6	0.86	1.20	5.0	0.47	30.2	24.9	4.87	1.34	4.18	14.12	0.0091
1350.0	38.8	0.97	1.36	4.8	0.50	18.3	20.9	3.89	1.16	3.41	8.93	0.0145
1350.7	38.8	1.03	1.25	4.7	0.47	18.3	19.8	3.55	1.06	3.11	8.74	0.0134
1352.0	40.2	0.81	1.11	4.4	0.48	25.3	28.5	4.15	1.31	3.23	10.65	0.0097
1352.8	70.2	0.59	1.28	6.1	0.43	31.4	39.6	11.58	4.33	10.85	31.05	0.0195
1370.4	74.8	0.76	1.41	6.9	0.52	49.0	43.5	14.72	5.33	11.85	28.19	0.0179
1392.9	1.11	0.04	0.02	0.1	0.01	2.8	1.2	0.19	0.08	0.21	0.18	0.0020
1400.2	68.17	0.80	1.18	5.6	0.49	27.3	38.3	17.69	5.69	12.89	8.30	0.0169
1420.1	82.12	1.06	1.93	9.1	0.67	63.2	49.9	16.70	5.59	12.26	35.06	0.0198
1429.7	62.8	0.90	1.42	5.4	0.41	29.1	33.2	15.79	2.91	10.22	3.66	0.0212
1440.6	53.2	0.47	1.00	4.8	0.36	22.3	30.5	14.67	2.90	9.33	2.84	0.0162
1450.6	4.4	0.15	0.15	0.5	0.03	11.3	2.7	0.93	0.17	0.37	0.66	0.0287
1460.2	53.2	0.36	0.86	4.9	0.40	25.0	35.7	17.28	2.52	10.06	3.02	0.0278
1470.0	53.9	0.47	1.04	5.2	0.40	33.1	32.7	16.33	2.76	8.99	2.29	0.0471