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RELATIONSHIP OF THE MAGNESIUM/CALCIUM RATIO
TO THE STRUCTURE OF
THE REYNOLDS AND WINFIELD OIL FIELDS
MONTCALM COUNTY, MICHIGAN

by
David Lewis Egleston

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ABSTRACT

Geologists have long known from studies of outcrops that zones of weakness in solid carbonate rocks give rise to conditions that are conducive to secondary dolomitization. It is only natural that secondary dolomitization should occur along bedding planes, seams, joints, fractures or faults. More recently the idea of tension fractures along the apices of folds being dolomitized or even of dolomitization occurring at the apex of the fold without fractures in subsurface structure has been proposed. To understand better these possible relationships, it was decided to analyze samples of a carbonate-producing formation with adequate subsurface structural control.

The Reynolds and Winfield Oil Fields of Montcalm County, Michigan, were selected for this study. The versenate method of titration was used to determine the amount of magnesium and calcium present in the prepared

samples. This comparatively recent method gives accurate and fairly rapid results. These results as used in this report are based on the atomic ratio with the weight ratio also tabulated. The magnesium to calcium atomic ratios were plotted on base maps for certain intervals and contoured in the form of ratio maps. By comparing the ratio maps to the structural map of the fields a definite pattern or relationship should exist if dolomitization exists along the apices of folds. In this study there was no recognizable relationship between the ratio maps and the structure maps.

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INTRODUCTION

General:

The occurrence of secondary dolomite or dolomitic limestone adjacent to zones of weakness has been noted by many authors. Steidtmann (1917, p. 448) in his paper on the origin of dolomites states that secondary dolomites can be recognized by their relation to faults, fissures, and their secondary openings. Also as noted in Lauer (1917, p. 455) in his discussion of cavities showing some alignment:

It is also of interest to observe that most of the openings show a rough alignment, or are confined to a well-defined zone, as if they were the result of solution by waters travelling along a seam, joint, or bedding plane. This fact strongly suggests the presence generally throughout the limestone of enlarged open spaces along induced joints and cracks.

In Indiana, Ohio, and particularly in Michigan, a considerable number of petroleum fields produce from porous zones in apparently locally dolomitized limestones. In a study of the development of porosity through dolomitization, Landes (1946, pp. 305-318) paid particular attention to the relationship of the dolomitized zones to fissures, faults and fractures. In two of the fields

which he used as examples (Adams and Deep River pools of Arenac County, Michigan), the dolomitized zones extended for several miles in straight narrow bands not coincident with structures. Landes believed that there still was a relationship between the position of the dolomite body and structure. In explaining the porosity that is confined to locally dolomitized zones in limestone, he concluded that:

.....local diastrophism has produced master fissures in the limestone containing section; that an artesian circulation has been developed which has carried waters through deeper dolomite and up into the limestone; and that these waters have replaced some of the limestone by dolomite that is locally porous where there was an excess of solution over precipitation during the replacement process.

As a result of this study, Landes recommended that well samples be analyzed for magnesium carbonate content and indicated that the presence of approximately 40 per cent by weight indicates ample porosity and might well be the basis for lateral drilling in the hope of finding true dolomite. Landes also cites Carman and Stout who express the belief concerning the Trenton reservoir in Ohio that at least 20 per cent of magnesium carbonate is necessary for oil production.

Jodry (1954, pp. 38 and 39) expressed the belief that folded structures could be dolomitized on the apices

of the folds, as well as along faults and fissures, as the result of ascending waters. His study of dolomitized zones in the Rogers City Formation in Mecosta County in central Michigan, tends to bear out this belief.

Application of the versenate method for determining calcium and magnesium and the mapping of the magnesium to calcium ratios thus obtained, resulted in a lithologic ratio map of the area which coincides closely with a subsurface structural contour map of the formation. With the data from 44 wells that penetrated the Rogers City Formation, plus the data obtained from 45 shallower wells, Jodry (1954, p. 4) stated that at least five separate structural interpretations were possible.

In order to determine more exactly the nature of a possible relationship between the magnesium to calcium ratio and structure in a dolomitized limestone formation, it was decided to apply the versenate method of determining calcium and magnesium, and subsequent mapping of the magnesium to calcium ratios, to the study of an area with adequately controlled structure from which samples would be available.

If the assumption that dolomitization occurs along tension fractures developed on the apices of folds holds true, the atomic ratio interval map and the structure

contour map should show conformity. That is, the location of tension fractures and possibly faults on the structure highs or lows should reflect a pattern on the atomic ratio map. A high magnesium to calcium atomic ratio (possible maximum 1.00) should exist on the structural center and to the sides the ratio should approach 0 in the limestone.

Resume of Dolomites:

The generally accepted theories of the origin of dolomites are here summarized. (See Bibliography on Dolomites) Although the literature available is voluminous and conflicting in some aspects, the modes of formation and description of dolomite generally agreed upon can be classified into three types. (The following summary of dolomitic types is essentially taken from Chilingar, (1956c, p. 2489).)

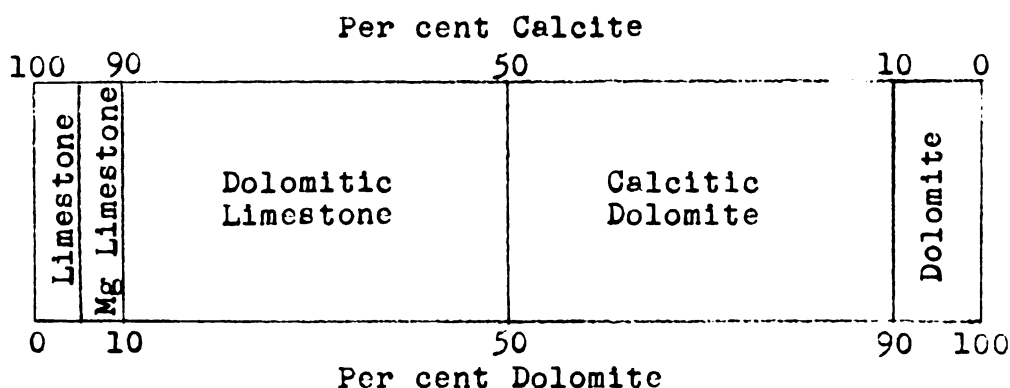
1. Primary dolomites: Primary dolomites are those formed by chemical precipitation of $MgCa(CO_3)_2$ from a standing body of water. They are easily recognized when associated with other sediments. They are well stratified, occupy definite stratigraphic horizons, are very fine-grained, many have coagulating centers, possess characteristic microlayering, and very rarely contain indigenous fossils. These dolomites lack

primary porosity and caverns, and are commonly interlayered with clays, marls, and gypsum. Dolomite commonly occurs as pseudomorphs after gypsum.

2. Diagenetic dolomites: Diagenetic dolomites are those formed by the interaction of the lime carbonate sediment and magnesium bearing sea water, presumably before appreciable burial. They can be found as layers or lenses with obscure stratification. They have slight porosity and fine-grained texture with xenoblastic grains whose outlines are impressed by adjacent crystals. These are of irregular form, and are filled with dust-like inclusions. Relict structure is commonly evident, and the fossil remains are in the form of molds.
3. Epigenetic dolomites: The epigenetic dolomites result from alteration of completely lithified limestones by percolating meteoric solutions or hydrothermal solutions. Epigenetic dolomites are cavernous, have obscure stratification, patchy distribution of dolomite, non-uniform grain size, and relict structure. Idiomorphic rhombohedrons of dolomite with a nucleus and

surrounding zones are common. The texture is not uniform and the original fauna remain in the form of molds. The calcium to magnesium ratio of epigenetic dolomites varies widely over short distances, both vertically and horizontally.

Carbonate rocks contain various mixtures of the minerals dolomite ($\text{MgCa}(\text{CO}_3)_2$) and calcite (CaCO_3). From Pettijohn (1957, p. 417), the terminology of the end members with gradations are shown below.



The magnesium to calcium ratio used in this report is on the atomic basis. Therefore, a rock with an atomic ratio of .75 would be the same as a rock with 75 per cent dolomite and 25 per cent calcite and is called a calcitic dolomite. In a pure dolomite the rock would have one atom of magnesium to one atom of calcium for a ratio of one. A pure limestone would have one atom of calcium and no magnesium, so the ratio is zero.

SELECTION OF AN AREA

In order to understand the relationship of the magnesium to calcium ratio to a structure, a relatively small and closely drilled area is desirable, so that an intensive study can be made of the geologic data. Additional attributes include available well samples, ample data for contouring the subsurface structure, and preferably a petroleum producing zone which automatically implies porosity and permeability.

The area chosen contains the Reynolds and Winfield Fields in the northwest portion of Montcalm County, Michigan.

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SCALE OF MILES
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Figure 1. Regional location map of area under study

THE REYNOLDS AND THE WINFIELD OIL FIELDS

Location and Extent:

These fields are located in central Michigan and they include Winfield Township (Sec. 5, 6, 7, 8, 17, 18, 19, 20, 21, 28, 29 and 30, T12N, R9W) and Reynolds Township (Sec. 1, 2, 11, 12, 13 and 14, T12N, R10W). Also included in the area are Sec. 35 and 36, T13N, R10W of Aetna Township, Mecosta County, located directly north of Reynolds Township, Montcalm County. The main portion of the north end of the northwest trending anticline is approximately one mile south of the town of Morley, Mecosta County. The Winfield Field, which is located nearly two miles southeast of the Reynolds Field on the same anticline, is three miles east of Howard City, Montcalm County.

The producing area for the Reynolds Field is essentially in Sec. 6, 7, 17 and 18, T12N, R10W. It extends in a northwest-southeasterly direction for nearly three miles on the major axis of the structure and is approximately one mile wide. One exception to this trend is noted; there is a major producing zone which extends from the middle of the field in a northeast direction for 1 3/4 miles. In the case of the Winfield Field,

production is located in Sec. 20 and 26, T12N, R9W. Most of the production from both fields is located on the northeast or more steeply dipping flank of the anticline (see Figure 2). The total area drilled at the end of 1956 was 1350 acres for the Reynolds Field and 50 acres for the Winfield Field.

History of Development:

The small Winfield pool was first discovered in 1936 by the Daily Crude Oil Company, F. Weatherby #1, SW, SW, SE, Sec. 20, T12N, R9W, Permit No. 3519, the author's identification number 36. With a ten acre spacing pattern, this pool was not exploited because of low initial production and numerous dry holes on the structure. Sixteen holes were drilled on the structure or immediate area, but only five producers were developed with the production mainly found on the northeast flank of the southeast plunge of the anticline. Not until interest was renewed in this area in 1954 was the larger Reynolds Field discovered by McClure Oil Company, A. Kuhn #1, SE, SE, NW, Sec. 1, T12N, R10W, Permit No. 18813, the author's identification number 52, on the northwest side of the structure. Since then, to April, 1957, 59 holes have been drilled in the Reynolds Field, mostly on structure,

and 41 are producers. The area is still being developed on a forty acre spacing pattern. Most of the dry holes were drilled on fringe locations, but some dry wells are located on structure and are encircled by producers.

Production:

In general, Michigan oil wells are not prolific producers. The area under study is no exception but some wells have a natural flow of 70 barrels per day on reduced output. According to the Michigan Geological Survey (1956), cumulative production of the Reynolds Field to the end of 1956 amounted to 627,215 barrels of oil, of which 466,048 barrels were produced during 1956. This is rapidly becoming one of the largest producing fields in Michigan. Brine production amounted to 55 barrels per day, of which 33 were disposed of by subsurface and 22 by surface methods. The Winfield Field produced 688 barrels of oil in 1956 for a cumulative total of 67,955 barrels; 130 barrels of brine per day were also produced and returned to the subsurface. Recovery per acre drilled amounts to 465 barrels of oil for the youthful Reynolds Field and 1,359 barrels for the older Winfield Field.

Producing Zones:

All wells used in this report produce from the "Reed City Pay" of Middle Devonian age, although in this area three wells produce from the Traverse formation roughly 450 feet above this zone. Only one pay zone, approximately two feet thick, is known in the "Reed City Pay" which is located immediately under, or a few feet below, an anhydritic bed which may serve as the impermeable cap rock. The reservoir rock is characteristically dolomitic. (See lithology page 17) A definite oil-water contact has not been found, but the flow in most wells must be water-driven because of the high flowing water found in dry wells off the flanks. A very faint trace of gas is found in some wells which increases the fluidity of the oil.

Stratigraphy:

The Traverse group, with the Bell shale formation at its base lies immediately above the Rogers City-Dundee formation, as noted in the proposed subsurface stratigraphic column of Michigan from Landes (1951, p. 2), presented in Figure 3. Although easily recognizable on the eastern side of the Michigan basin, the Rogers City and Dundee formations in the west-central and western side of the Basin are relatively indistinguishable because

			Name of unit	Thickness in feet	Description	
DEVONIAN	Upper		Traverse group	100-875	Limestone and shale	
			Rogers City formation	0-125	Brown limestone	
			Dundee formation	0-400	Mostly limestone	
	Middle	Detroit River Group	Lucas form.		68-1124	Mostly light-colored dolomite and anhydrite, some salt
				Richfield member	0-80	Dolomite with sandstone locally
		Amherstburg form.		0-150	Mostly dark-brown to black limestone or dolomite	
			Filer sandstone lentil	0-100	Sandstone	
				0-200	Mostly dark to black limestone or dolomite	
			Sylvania sandstone member	0-300	Sandstone with minor dolomite and chert	
			Bois blanc formation	0-1000	Entirely cherty limestone or dolomite	
	Lower		Garden Island formation	0-30	Dolomite	
			Bass Island dolomite and Salina formation	84-5000	Dolomite, shale anhydrite, and salt	

Figure 3. Proposed nomenclature for a part of the sub-surface section of the Michigan basin.
(After Landes 1951, p. 2)

Remarks

Bell shale at base
EROSIONAL UNCONFORMITY
Absent in southern and southwestern Mich. Usually included in the Dundee formation in oil field nomenclature.
EROSIONAL UNCONFORMITY
Absent in southwestern corner of Michigan
EROSIONAL UNCONFORMITY
Anderon limestone, which overlies Lucas formation in southeastern Michigan, not recognizable in subsurface. Lower part of the Lucas of subsurface is equivalent to the Lucas of type locality. Upper part of the Lucas may be time equivalent of the Columbus limestone across Findlay arch in Ohio. Evaporite sequence of rocks of Lucas in subsurface is ordinarily referred to in oil field nomenclature as "Detroit River". The Detroit River group is also referred to as the upper Monroe by some geologists
Subsurface only, and mainly in central and western Mich. Dolomite of the Richfield member is principal Detroit River oil reservoir. "Freer sand" is a sandstone in the Richfield
EROSIONAL UNCONFORMITY
Absent in southwestern Michigan. Usually referred to in oil field as "Sylvania formation" or "Black Lime"
Erratic distribution; greatest thickness in Western Michigan
Absent in southwestern, western, northern, and northeastern Michigan
EROSIONAL UNCONFORMITY
Absent in southwestern and southeastern corners of Michigan
EROSIONAL UNCONFORMITY
Oriskany sandstone equivalent. Very patchy distribution
EROSIONAL UNCONFORMITY
Bass Island dolomite is referred to as the "Lower Monroe" by some geologists

of similar lithology, as noted by Cohee and Underwood (1945). In some areas the formations are designated as "Dundee" for the upper, or Rogers City formation, and "Dundee Restricted" for the lower or true Dundee formation. Approximately 70-85 feet below the top of the Rogers City-Dundee formation is a zone, 20-30 feet thick, of interbedded dolomite lenses and anhydrite; these are the uppermost strata of the Detroit River Group, according to Baltrusaitis, Kelly, et al (1948, p. 7). Immediately below or within a few feet below the base of the anhydrite is the porous dolomitic zone known as the "Reed City Pay". The dolomite extends downward for one hundred feet to another anhydrite bed which is the cap rock of the "Richfield Pay", not a producing zone in this area. The Detroit River Group continues downward through more dolomites, sandy dolomites, and sandstones, and its base rests unconformably on rocks of Silurian age.

The above descriptions are generally entrenched in the geologic literature of Michigan. T. S. Knapp (1947) wrote a short paper that took great exception to Cohee and Underwood (1945). Knapp writes that the Rogers City formation extends from the Bell shale to the top anhydrite bed, and the Dundee formation lies between the top anhydrite and the second or bottom anhydrite bed. If

Knapp's theories are correct, and they seem plausible, the rocks in the area under study would be changed from the Upper Detroit River Group to the Upper part of the Dundee Formation.

A further addition to the nomenclature is the stratigraphic parlance of the petroleum geologists who include everything between the Bell shale and the second or bottom anhydrite bed collectively within "Dundee". Everything below is called "Detroit River". This combination is due to the practically impossible task of distinguishing between the various lithologic units because of differences between outcrop and subsurface samples, local dolomitization, interfingering, transition zones, facies changes, and the fact that the anhydrites and two pay zones mentioned are present only in central and west-central Michigan and are not recognizable in Devonian outcrops to the north and southeast. The published and therefore generally accepted stratigraphic terms will be used throughout this report. Because of the distinct and easily recognized lithologic break between the Bell shale and the underlying Rogers City-Dundee formation, the latter is used as a contouring horizon by petroleum geologists. The structure contour map of the area under study (Figure 2) is contoured on this horizon.

Lithology:

The Rogers City-Dundee formation in this area is a gray to brown, fossiliferous limestone which is dolomitic in places.

The cap rock overlying the "Reed City Pay" is crystalline white anhydrite, approximately 20-30 feet thick, which appears to be interbedded with small beds and stringers of finely crystalline dolomite, anhydritic dolomite, and calcitic dolomite or possibly even dolomitic limestone. Vitreous, clear, pitted, well-rounded grains of quartz, some with a light yellowish stained appearance, were noted in the basal portion of the anhydrite.

In the "Reed City Zone" the dolomites or calcitic dolomites are unfossiliferous. The rock is characteristically a fairly dense, light tan to buff to dark brown dolomite with scattered pinpoint, intercrystalline and vugular porosity. In texture this rock varies extremely from crypto-crystalline through finely crystalline sucrosic to fairly coarse crystalline. The samples in the cuttings ranged from very fine pieces of rhombohedrons, small pieces, small chips exhibiting a slightly recemented (clastic?) appearance, and small fingernail-sized chips. While these features may be correlated between two or three neighboring wells, the author feels that this

matching is not possible over any great distance. In a few wells, small monoclinic crystals of selenite were noted. Also found in samples from two wells were small black styolitic partings.

An unusual occurrence of a very magnetic, black, granular substance was noted when separating the "scale" (rusty debris from metal pipe and casing) from the samples by an electromagnet. The ferric and ferrous ions present were determined by the ferro-cyanide method when first noted in place. By X-ray methods this substance was analyzed by R. E. Goodrich (1957) who identified it as magnetite. The amount of magnetite present in these few samples was estimated as 1 to 3 per cent by volume. This magnetite when first noticed was erroneously believed to be part of the scale, but in well number 66 small grains of magnetite were found toward the back of a vug nearly one-sixth of an inch in diameter within a dolomite chip one-third of an inch in diameter. This vug was surrounded on the outside rim by white crystals of dolomite.

After noting this peculiarity, the writer talked to M. Osgood, who stated that great difficulty was experienced in getting some wells to produce, particularly 20, 21, 25, 26, 64 and 66. These wells were analyzed by the Dow Chemical Company who informed Osgood that

much iron was present in these wells, thereby complicating production methods. This general area is essentially where most of the magnetite samples were obtained.

The occurrence of magnetite, as plotted in the tables in the sample interval column, falls within two feet up or down of the top of the pay zone. This would seem to indicate that the magnetite was introduced during the minor uplift of this area as explained on page 20.

Structure:

Generally, the structural configuration of these fields, as contoured on the top of the Rogers City-Dundee formation (Figure 2), resembles a doubly plunging anticline with 20 feet of absolute closure and a likelihood of 40 feet from the data available. The structure apparently is the result of cross folding with the major axis trending in a northwest-southeast direction and minor axis in a northeast-southwest direction. Some irregularities are noted near the top of the structure. The lower structural contours essentially outline the more definite trend. These minor irregularities therefore, appear to be unimportant. One minor structural saddle is located in Sec. 18 and 19, with another well-defined saddle located on the line between Sec. 7 and 18, all in

T12N, R9W. The structural alignment agrees with the dominant northwest-southeast structural trends in the central basin area as described by Cohee (1945).

To check the possibility of a supratenuous fold, a contour map was drawn on the pay zone or oil shows at equivalent depths (Figure 4). This shows agreement as to trend with the structure of the top of the Rogers City-Dundee formation. The thickness between the pay zone and top of the Rogers City-Dundee formation is approximately 92-95 feet on top of the structure, and 102-110 feet on the flanks. This variation indicates evidence of erosion or a possible mild uplift in this area during deposition of the Rogers City-Dundee formation. An isopach map (Figure 5) was constructed of the interval between the pay zone and the top of the Rogers City-Dundee formation. The thickness is 92-93 feet in Sec. 7 and 28 but increases to 110 feet in some places. The top of the Rogers City-Dundee dips very gently, but the depth to the pay zone increases more rapidly, thereby suggesting gentle erosion, rising, or folding before the Rogers City-Dundee formation was deposited. Thus the age of mild folding or erosion is considered to be Middle Devonian.

As a check on the possible age of the major folding, a contour map was made of the top of the Traverse

limestone (Figure 6) of Middle Devonian age which is stratigraphically about 450 feet above the top of the Rogers City-Dundee formation. These maps showed agreement as to trend, even to the northeast extension on the minor axis of the Reynolds Field. One small difference noted was the major axis of the anticline at the Traverse limestone horizon had a slightly more westerly trend. The age of more intense folding is considered to be post-Mississippian inasmuch as Young (1955, p. 11) found that the Traverse limestone structure was reflected in the Coldwater formation of Mississippian age.

ANALYTICAL METHOD

Schwartzzenbach, in 1947, reported the results of a series of investigations of the complex ions of the alkaline-earths and suggested the use of ethylene-diaminetetra-acetic acid (commonly called versene) as a titrant for the sum of calcium and magnesium in water and soils by using Eriochrome Black T (F 241) as the indicator. This, with certain modifications by other chemists, has become a great time-saving method in analyzing for calcium plus magnesium in limestones and dolomites. Previously the methods available involved the staining of the sample with silver chromate, Lemburg's solution, or potassium ferricyanide which required polished slabs or thin sections and, after staining, detailed examination to determine the amounts of calcite and dolomite present. Or the analysis could be made by using the time-consuming method of precipitation and separation of the two in solution.

Further work and modifications by Banewicz and Kenner (1952, p. 1186); Cheng, Kurtz, and Bray (1952, p. 1640); and Gehrke, Affsprung, and Lee (1954, p. 1944) perfected the analytical technique so that calcium could be determined separately by using Murexide as the

indicator. The amount of magnesium present in the sample is determined by subtracting the calcium from the total calcium and magnesium present. Also, the aforementioned versene was modified to disodium dihydrogen ethylenediaminetetra-acetate dihydrate. Results obtained with the versenate titration in analyzing standard samples were in excellent agreement with results obtained by conventional procedures.

The materials necessary, preparation of the solutions, standardization of solutions, and procedure of analyses are essentially those described by Cheng, Kurtz and Bray.

Samples

Source:

Core chips or outcrop specimens are best for analysis because of known position or location and lack of contamination by cavings. Rotary samples are the least dependable to work with because of the difficulty in locating the sample depth. Also, the required amount of sample might not be available in the first sample show. The continuous intermixing and powdering with additional contamination as the sample comes up the bore makes analyses undependable. Cable tool samples are better located with respect to depth. They are also relatively

pure samples if chips are available. Fortunately in the area under study, cable tool samples were available so that the depths are relatively correct. Because the pay zone was located almost immediately below the anhydrite, the casing was set approximately at the base of the anhydrite, increasing the amount of foreign material in the uppermost samples. Deep samples into the pay zones were not available in all wells because drilling usually ceased as soon as oil was encountered. If the stratigraphy, lithology, and drilling practices of an area are well known to the analyst, foreign material in the sample is quite easily determined, either from empirical data, homogeneity of grain size, or from the sporadic occurrence of such material in the section.

Preparation:

The samples were first thoroughly washed and dried. Pieces of casing and other foreign material were removed and a magnet passed through the sample to pick up any pieces of contaminating iron which were present. If only a ratio of magnesium to calcium, instead of exact amounts is desired, cherts and other relatively inert materials of a non-limy nature do not have to be separated before analysis. The ratio of magnesium to calcium will still

remain the same, but the percentage amount of dolomite and calcite present will be slightly different. The one gram samples used in this work were crushed by mortar and pestle to aid in complete and rapid digestion in hydrochloric acid (1:1) instead of perchloric acid as recommended by Cheng, Kurtz and Bray.

Calculations

If one gram of sample is dissolved in a 250 milliliter solution, and a 10 milliliter aliquot is taken for titration, calcium and magnesium can be calculated as follows:

$$\frac{A \times 1.4 \times B}{1/25 \text{ g} \times 1000 \text{ mg/g}} \times 100 = A \times B \times 1.4 \times 2.5 = \% \text{ CaO}$$

$$\frac{C \times 1.66 \times (D-B)}{1/25 \text{ g} \times 1000 \text{ mg/g}} \times 100 = C \times (D-B) \times 1.66 \times 2.5 = \% \text{ MgO}$$

A = milligrams of calcium per milliliter of versenate solution

B = milliliters of versenate solution used in titration, with Murexide as indicator

C = milligrams of magnesium per milliliter of versenate solution

D = milliliters of versenate solution used in titration, with F-241 as indicator

If the weights and measures are made with reasonable care in the preparation of the standard calcium solution and

in the preparation of the versenate solution, the quantities "A" and "C" tend to become constant in the formula. The results were identical in the standardization made by the writer, using the same standard calcium solution and successive solutions of versenate. The standard calcium solution prepared contains one milligram of calcium per milliliter of solution. A and C are calculated as follows:
 $A = 10 \text{ mg. calcium (soln)} / 23.6 \text{ ml versenate} = 0.424 \text{ mg.}$

Ca/ml

$$C = 0.424 \times 0.607 \frac{(A.W. \text{ Mg} - 24.32)}{(A.W. \text{ Ca} - 40.08)} = 0.257 \text{ mg. Mg/ml}$$

Using the above as constants, the formulae listed at the beginning become greatly simplified as follows:

$$\frac{0.424 \times 1.4 \times B \times 100}{1/25 \text{ g} \times 1000 \text{ mg/g}} = B \times 1.48 = \% \text{ CaO}$$

$$\frac{0.257 \times 1.66 \times (D-B) \times 100}{1/25 \text{ g} \times 1000 \text{ mg/g}} = (D-B) \times 1.07 = \% \text{ MgO}$$

By using gravimetric constants, the MgO times 0.60317 and CaO times 0.71469 give the percent by weight of magnesium and calcium if desired.

Ratios

Selection:

Since the purpose of this study is to see the relationship between the magnesium to calcium ratio and structure, it is desirable to present these analyses as

figures so they can be used as contour control points. There are two methods of presenting this data - by weight or on an atomic basis. The magnesium to calcium ratio by weight will vary from .607 (in a normal dolomite) to zero (in a pure limestone). On an atomic basis, the magnesium to calcium ratio varies from 1.000 in a normal dolomite to zero in a pure limestone. Since it is evident from a study of the formula for dolomite that the magnesium to calcium atomic ratio for $\text{MgCa}(\text{CO}_3)_2$ is 1, it would appear that a presentation of the atomic ratio would more clearly show the extent of dolomitization than a weight ratio, since it is not immediately evident that the magnesium to calcium weight ratio for dolomite is .607.

Calculations:

The magnesium to calcium ratio can be calculated from the percentages of each oxide by multiplying by the gravimetric factor which will give the magnesium to calcium ratio by weight as follows:

$$\frac{\% \text{MgO}}{\% \text{CaO}} \times 0.843 = \frac{\text{Mg}}{\text{Ca}} \text{ ratio by weight}$$

To convert the magnesium to calcium ratio by weight to a ratio of number of atoms it is necessary to multiply the first magnesium to calcium ratio by the conversion factor 1.648 as follows:

$$\frac{\% \text{Mg}}{24.32} = \text{Mg At.} \qquad \frac{\% \text{Ca}}{40.08} = \text{Ca At.}$$

$$\text{So } \frac{\frac{\% \text{Mg}}{24.32}}{\frac{\% \text{Ca}}{40.08}} = \frac{\% \text{Mg}}{\% \text{Ca}} \times \frac{40.08}{24.32} = \frac{\% \text{Mg}}{\% \text{Ca}} \times 1.648 = \frac{\text{Mg}}{\text{Ca}} \text{ by atomic basis}$$

Although both methods will give equally good results as to contourability, contouring in this report was on the atomic basis. The magnesium to calcium ratio by weight is tabulated along with the atomic ratio in Table 1.

Notes Describing Tables

Columns read from left to right

Permit Number	- Issued by Michigan Geological Survey
Well Name	- Self explanatory
Location	- Self explanatory
Elevation	- Self explanatory
Top of Rogers City-Dundee	- All elevations are minus sea level data
Top of Traverse Limestone	- All elevations are minus sea level data Void - could not be picked
Top of Pay Zones or Shows	- All elevations are minus sea level data Void - could not be picked P - producing A - abandoned D - dry
Identification Number	- This author's
Sample Interval	- All elevations are minus sea level data Void - insufficient or no samples available M - magnetite noted
By Weight Mg/Ca Ratio	- Self explanatory
Atomic Mg/Ca Ratio	- Self explanatory

TABLE 1

Permit Number	Well Name	Location	Ground Elev.	Top of Rogers City-Dundee
MONTCALM COUNTY Winfield Township, T12N, R9W				
19991	J. Dennis #1	SE,NW,SW-5	958	-2332
19985	Mich. Consolidated Gas Co. No. 2	SE,SW,NE-6	941	-2328
19992	N. F. Croff #1	SE,NE,SW-6	938	-2324
20326	J. Baxter #1	SE,NW,SW-6	939	-2325
20099	A. Weikert No. 1	SE,SW,SW-6	921	-2322
20335	A. Weikert #2	SE,SE,SW-6	925	-2318
20085	D. C. Blair No. 1	CS $\frac{1}{2}$,NE,SW-6	946	-2326
19892	Mich. Consolidated Gas Co. No. 1	SE,NW,SE-6	941	-2326
19993	J. Staffen No. 1	SE,SW,SE-6	930	-2322
20277	John & Florence Nicholson No. 1	SE,SE,SE-6	929	-2326

Top of Traverse Limestone	Top of Pay Zones or Shows	Identi- fication Number	Sample Interval	By Weight Mg/Ca Ratio	Atomic Mg/Ca Ratio
-1887	-2433 D	1A	-2430-33	.46	.76
		B	-2433-37	.54	.89
		C	-2437-39 M	.55	.91
-1878	D	2A	-2420-26	.56	.92
		B	-2426-30	.56	.92
		C	-2430-35	.56	.92
-1867	-2422 P	3			
-1866	-2422 P	4A	-2420-21	.36	.59
		B	-2421-25	.58	.96
-1866	-2418 P	5A	-2409-11	.37	.61
		B	-2411-13	.27	.45
		C	-2413-14	.35	.58
		D	-2414-17	.34	.56
		E	-2417-19	.37	.61
-1867	-2411 P	6			
-1872	-2424 P	7A	-2411-16	.32	.53
		B	-2416-19	.35	.58
		C	-2419-24	.41	.68
-1873	-2421 P	8	-2418-22	.43	.71
-1875	-2426-29 D	9A	-2418-21	.48	.79
		B	-2421-23 M	.58	.96
		C	-2423-26 M	.56	.92
		D	-2426-29	.607	1.00
-1876	-2434 P	10A	-2422-29	.54	.89
		B	-2429-35	.60	.99

Permit Number	Well Name	Location	Ground Elev.	Top of Rogers City-Dundee
20334	J. Staffen #2	SE,NW,NE-7	920	-2319
20333	A. Schnick A-1	SE,SW,NE-7	916	-2326
19827	W. Jack #2	SE,NE,NW-7	930	-2310
5130	A. L. Jacks Estate #2	NE,NW,NW-7	927	-2327
19919	W. Jack No. 1	SE,NW,NW-7	930	-2317
19926	R. Weikert No. 1	SE,SW,NW-7	917	-2309
20249	R. Weikert No. 2	SE,SE,NW-7	916	-2314
20196	Schnick No. 3	SE,NW,SW-7	915	-2323
20095	Frank Schnick No. 1	SE,NW,SE-7	922	-2315
20146	F. Schnick No. 2	SE,SW,SW-7	913	-2329
20258	A. Weatherby	SE,SW,SE-7	912	-2330
20004	Lint Heirs No. 1	SE,SW,NE-8	942	-2347
2380	J. K. Knapp No. 1	CE $\frac{1}{2}$,SE,NE-17	930	-2339

Top of Traverse Limestone	Top of Pay Zones or Shows	Identification Number	Sample Interval	By Weight Mg/Ca Ratio	Atomic Mg/Ca Ratio
-1873	-2413-14 P	11A B	-2410-13 -2413-16	.45 .607	.74 1.00
-1864	-2423 P	12A B C	-2416-21 -2421-23 -2423-24	.46 .54 .58	.76 .89 .96
-1870	-2406 P D	13 14	-2403-05	.37	.61
-1866	-2411 P	15			
-1837	-2405 P	16	-2403-07	.59	.97
-1858	-2409 P	17			
-1861	-2415-18 P	18A B	-2412-13 -2413-17	.36 .57	.59 .94
-1859	-2407 P -2427 D	19A B 20A B C D	-2403-05 M -2405-07 M -2423-25 -2425-27 -2427-28 -2428-30	.40 .42 .46 .55 .54 .53	.66 .69 .76 .91 .89 .87
-1852 ?	-2428 P	21A B	-2425-28 -2428-29	.46 .607	.76 1.00
-1885	-2440 D	22A B C D	-2440-45 -2444-49 -2449-54 -2454-59	.56 .59 .607 .60	.92 .97 1.00 .99
-1880 ?	-2437 D	23A B C D E F	-2418-26 -2426-30 -2430-34 -2434-37 -2437-41 -2441-44	.41 .36 .46 .607 .58 .56	.67 .60 .77 1.00 .96 .92

Permit Number	Well Name	Location	Ground Elev.	Top of Rogers City-Dundee
20325	Olson #1	SE,NW,SW-17	920	-2324
20246	Crimmins No. 3	SE,NE,NE-18	916	-2323
20186	Marshall, Steven & Merel Lovegran #2	SE,NW,NE-18	914	-2320
20193	Charles Buck No. 1	SE,SW,NE-18	920	-2318
20233	Charles Buck No. 2	SE,SE,NE-18	916	-2320
20130	Marshall Steven & Merel Lovegran #1	SE,NE,NW-18	916	-2319
20037	Catharine L. Crimmins No. 1	SE,NW,NW-18	912	-2317
20248	Lovegran-Marshall No. 3	SE,SE,NW-18	915	-2308
13616	E. A. Jones et al No. 1	SW,NE,SE-18	917	-2316
19635	Frank & Daisy Terwilliger No. 1	NE,NE,SE-19	915	-2311

Top of Traverse Limestone	Top of Pay Zones or Shows	Identification Number	Sample Interval	By Weight Mg/Ca Ratio	Atomic Mg/Ca Ratio
-1866	-2423-25 P	24A	-2414-20	.33	.54
		B	-2420-24	.57	.94
		C	-2424-27 M	.55	.91
-1867	-2424 P	25A	-2421-24	.50	.82
		B	-2424-26 M	.55	.91
		C	-2426-27	.57	.94
-1866	-2420 P	26			
-1872	-2419 P	27A	-2416-18	.43	.71
		B	-2420-23	.59	.97
		C	-2423-25	.56	.92
-1869	-2421-23 P	28	-2419-22	.46	.76
-1869	-2422 P	29A	-2414-16	.30	.49
		B	-2416-18	.34	.56
		C	-2418-20	.37	.61
		D	-2420-22	.52	.86
-1870	-2418-20 P	30A	-2415-18	.45	.74
		B	-2418-19	.60	.99
		C	-2419-20	.607	1.00
-1871	-2420 P	31A	-2410-14	.40	.66
		B	-2414-18	.44	.73
		C	-2418-21	.607	1.00
		D	-2421-24	.607	1.00
		E	-2424-25	.57	.94
-1872	D	32A	-2415-21	.43	.71
		B	-2421-29	.57	.94
		C	-2429-36	.55	.91
		D	-2436-44	.57	.94
		E	-2444-49	.58	.96
		F	-2449-53	.59	.97
-1873	D	33A	-2411-13	.38	.63
		B	-2413-15	.40	.66
		C	-2415-17 M	.38	.63

Permit Number	Well Name	Location	Ground Elev.	Top of Rogers City-Dundee
3936	F. C. Voss No. 1	SE, SE, SW-20	915	-2310
4778	F. Weatherby No. 2	NE, NW, SE-20	936	-2319
3519	F. Weatherby No. 1	SW, SW, SE-20	900	-2313
8926	Weatherby et al #5	NW, SE, SE-20	943	-2312
8039	F. Weatherby et al No. 3	SW, SE, SE-20	934	-2314
8636	Weatherby No. 4	SE, SE, SE-20	906	-2327
19128	R. Hughes No. 1	SW, NW, SW-21	910	-2334
4431	Wm. Weatherby No. 1	NW, NW, NE-28	902	-2333
8434	Buggart #1	SW, NE, NW-28	898	-2331
19504	Eickenroth & Lean No. 1	SE, SE, SW-28	914	-2342
20032	Mary Hart No. 1	SE, NE, SE-28	928	-2344
3505	Eghotz No. 1	SW, SE, SE-28	901	-2344
8408	E. Parker No. 1	NE, NE, NE-29	925	-2322
4008	H. Parker No. 1	NW, NW, NE-29	907	-2313

Top of Traverse Limestone	Top of Pay Zones or Shows	Identi- fication Number	Sample Interval	By Weight Mg/Ca Ratio	Atomic Mg/Ca Ratio
-1865	D	34A	-2410-16	.55	.91
		B	-2426-32	.56	.92
		C	-2432-39	.58	.96
		D	-2439-43	.607	1.00
		E	-2443-51	.60	.99
		F	-2451-60	.59	.97
		G	-2460-70	.53	.87
		H	-2470-89	.58	.96
		I	-2489-99	.607	1.00
		J	-2499-2505	.31	.51
	D	35			
-1870	-2410 P	36			
-1871	-2417 P	37			
-1876	-2420 P	38			
-1881	-2430 P	39			
-1871	-2434 D	40A	-2430-33 M	.27	.45
		B	-2433-35	.607	1.00
		C	-2435-41	.59	.97
-1878	-2438 D	41	-2434-41	.49	.81
-1883	-2428 D	42			
-1890	-2436-37 P	43A	-2427-31	.39	.64
		B	-2436-37	.55	.91
-1905	-2450 D	44	-2446-50	.47	.78
-1894	-2445 A	45			
-1880	-2415 D	46			
-1877	-2420 D	47			

Permit Number	Well Name	Location	Ground Elev.	Top of Rogers City-Dundee
14254	Carl Matz No. 1	SW, NE, SW-30	907	-2318

Reynolds Township, T12N, R10W

19249	Amie Anderson No. 1	SE, NE, NW-1	914	-2333
19250	A. Kohn No. 2	SE, NW, NW-1	911	-2329
19414	A. Kohn No. 3	SE, SW, NW-1	908	-2325
18813	A. Kohn No. 1	SE, SE, NW-1	913	-2329
19008	J. Long No. 1	SE, NE, SW-1	902	-2323
19713	J. Long No. 2	SE, NW, SW-1	900	-2324
16437	A. Williams No. 1	SE, NW, SE-1	913	-2330
19537	Long Estate No. 1	SE, SE, SW-1	906	-2325
19829	O. M. Hansen	SE, SW, SE-1	917	-2319
19920	O. M. Hanson No. 1	SE, SE, SE-1	914	-2319
19565	Kohn No. A-1	SE, SE, NE-2	901	-2327
19016	Frank L. & Nellie O. Forest & Peter & Ima Nelson No. 1	SE, NE, NW-11	903	-2322
19828	Underwood et al No. 2	SE, NE, NE-12	920	-2319
16436	Underwood et al No. 1	SE, NW, NE-12	914	-2321

Top of Traverse Limestone	Top of Pay Zones or Shows	Identi- fication Number	Sample Interval	By Weight Mg/Ca Ratio	Atomic Mg/Ca Ratio
-1881	-2422 D	48A	-2414-16	.34	.56
		B	-2416-22	.54	.89
		C	-2422-27	.47	.78
		D	-2427-29	.45	.74
		E	-2429-33	.56	.92
		F	-2433-39	.56	.92
-1871	-2430 D	49			
-1873	-2427 P	50			
-1865	-2422 P	51			
-1869	-2423 P	52A	-2402-09	.31	.51
		B	-2409-15	.40	.66
-1870	-2426 P	53			
-1868	-2422 P	54			
-1874	-2432 P	55	-2405-18	.40	.66
-1868	-2428 A	56			
	-2414 P	57A	-2409-11	.38	.63
		B	-2411-14	.45	.74
-1876	-2417 P	58			
-1874	-2429 P	59			
-1871	D	60			
-1871	-2414 P	61			
-1872	-2414 P	62			

Permit Number	Well Name	Location	Ground Elev.	Top of Rogers City-Dundee
20008	Long Estate No. 3	SE,SW,NE-12	911	-2316
19918	C. Crimmins No. 1	SE,SE,NW-12	912	-2313
19802	James U. & Stella Long No. A-1	SE,SW,NW-12	909	-2321
19048	E. Maude Halladay No. 1	SE,NE,SW-12	917	-2315
19046	E. Maude Halladay No. 1	NW,NW,SE-12	909	-2324
20132	E. Maude Halladay No. 2	SE,SE,SE-12	909	-2320
20245	C. Crimmins No. 2	SE,NE,NE-13	906	-2323
9721	Von-Klein Smid No. 1	C-SE,SE-13	903	-2322
19391	C. E. Sorensen No.1	SE,SE,SW-14	900	-2337
MECOSTA COUNTY				
Aetna Township, T13N, R10W				
19095	Lineback No. 1	SE,NW,NE-35	889	-2330
19497	Zierke No. 1	SE,SW,SE-35	907	-2333
20030	Raby #1	SE,SW,SW-36	915	-2334

Top of Traverse Limestone	Top of Pay Zones or Shows	Identi- fication Number	Sample Interval	By Weight Mg/Ca Ratio	Atomic Mg/Ca Ratio
-1875	-2418 P	63			
-1869	-2408 P	64A B	-2401-04 -2404-06	.37 .44	.61 .73
-1870	-2432-40 D	65A B C	-2416-26 -2426-32 -2432-40	.36 .51 .60	.59 .84 .99
-1850	-2413-16 P	66A B C D E	-2401-03 -2403-05 -2413-14 M -2414-16 -2416-16½	.37 .51 .607 .54 .59	.61 .84 1.00 .89 .97
-1873	-2420 D	67A B C D E F	-2420-23 -2423-26 -2426-28 -2428-31 -2431-34 -2434-35	.46 .49 .56 .59 .57 .57	.76 .81 .92 .97 .94 .94
-1855	-2422-23 P	68A B	-2419-20 -2420-22	.42 .56	.69 .92
	-2417-18 P	69	-2424-26	.56	.92
-1880	D	70A B	-2397-2410 -2410-21	.34 .56	.56 .92
-1886 ?	D	71			
-1872	D	72A B C D	-2430-33 -2433-37 -2437-40 -2440-44	.38 .33 .35 .56	.63 .54 .58 .92
-1868	D	73			
	-2429 P	74	-2428-29	.54	.89

Permit Number	Well Name	Location	Ground Elev.	Top of Rogers City-Dundee
20310	Wm. Hill #1	SE, SE, SE-36	953	-2332

Top of Traverse Limestone	Top of Pay Zones or Shows	Identi- fication Number	Sample Interval	By Weight Mg/Ca Ratio	Atomic Mg/Ca Ratio
	D	75A	-2435-38	.51	.84
		B	-2438-43	.56	.92
		C	-2443-52	.59	.97
		D	-2452-59	.607	1.00

REPRODUCIBILITY OF DATA

The results obtained by this method have been checked by Cheng, Kurtz and Bray (1952, p. 1641) against known standards, and excellent results were obtained.

As a further check, the writer decided to analyze several samples from well number 10 (2429-35). All of the available sample was pulverized, as with all samples, and stirred. Six one-gram samples were taken separately and analyzed separately. The results are given in Table II.

TABLE II

Number	By Weight		$\frac{\% \text{ MgO}}{\% \text{ CaO}}$	Atomic Mg/Ca Ratio
	% MgO	% CaO	% CaO	
1	20.87	29.53	.7067	.987 or .99
2	20.92	29.38	.7120	.987 or .99
3	20.82	29.23	.7123	.987 or .99
4	20.92	29.45	.7104	.987 or .99
5	20.87	29.45	.7087	.987 or .99
6	20.92	29.38	.7120	.987 or .99

Although the ratio results were outstanding as to reproducibility, it is noted that the values in the CaO and MgO columns, and also the ratios of % MgO/ % CaO differ. These differences are so small that it is eliminated in the calculation of the atomic ratio to two significant decimals.

EVALUATION OF DATA

Vertical Extent of Dolomitization:

The magnesium to calcium ratios of the samples tested ranged from a low of .45 to a high of 1.00. These values range in rock types from a dolomitic limestone through a calcitic dolomite to a pure dolomite. Most of the ratios are in the higher figures. The lower values obtained are usually found near or in the interbedded dolomites and anhydrites above the pay zone. It seems that lower value carbonates should be present in this zone because of the large amount of calcium available for precipitation as calcium sulfate and consequently more calcium available for more limy carbonates.

Lateral Extent of Dolomitization:

The lateral extent of the mapped atomic ratio interval does not exhibit a large range of values. Most rocks are highly calcitic dolomites and dolomites.

Dolomitization in Producing Zones:

Samples through the producing zones were unfortunately not available in all wells. This is because the high pressures encountered in some areas caused blowouts of samples up the bore and the impracticability of drilling

deeper after a fairly good producer is found. Analyses of the producing wells as compared to dry wells in the same area do not reveal any change in the magnesium to calcium ratio. Dry holes on the flanks do not exhibit any difference as compared to the producing wells nearer the center. The only explanation that can be given for non-producers on the crest is that porosity is lacking, possibly due to compaction or recrystallization, or possibly pore-filling by magnetite as noted on page 18.

RELATIONSHIP OF DOLOMITIZATION TO STRUCTURE

Selection of Intervals:

The intervals selected for plotting of the atomic ratios were the first and second foot intervals of the pay zone; deeper intervals could not be plotted because of insufficient samples, as mentioned on page 45. The analyses of individual deeper wells both on the crest and the flanks of the anticline indicate that it is still highly dolomitic vertically and laterally.

The atomic ratios as plotted on the areal base map for the first foot (Figure 7) and the second foot (Figure 8) can have slightly variable contour interpretations. The author feels that the ratio maps as presented have the best general inclusive interpretation. In areas of low sample density, the atomic ratio above or below the specific datum was used, but only as a guide point.

Comparison of Intervals:

From examination of Figures 7 and 8, it can be seen that no elongate patterns are present. Generally the areas of pure dolomite are of a circular nature. Comparing the two figures, the relationship of slight stratigraphic units such as layers or lenses is brought out. Although

some differences are noted, this is probably due to the drill penetrating two different zones. The lateral extent of high dolomite is limited by areas of calcitic dolomite.

Comparison of Intervals to Structure Map:

Any relationship between the interval maps (Figures 7 and 8) and the structure map (Figure 2) should be seen by superimposing each map separately on the structure map. No relationship is noted. The dolomite areas are not elongated and are also not on the apex but are scattered throughout the area, generally on the eastern and north-eastern flanks with one possible area on the western flank. One area is also noted on the far west side.

Conclusions:

The results of this study based on the few samples available from a relatively thin interval do not verify the theory that dolomitization occurs along tension fractures following the apex of the fold nor that dolomitization occurs at the apex due to ascending water without the benefit of fractures. As evidenced by the analyses, this is a highly calcitic dolomite and dolomitic area. The interval maps do not reflect the subsurface structure contour map. It would appear therefore that secondary dolomitization and structure are not related in this area.

RECOMMENDATIONS FOR FURTHER STUDY

The occurrence of magnetite in the dolomitic rocks under study was of particular interest. If a core could be obtained from this area, particularly in the most southeasterly center of Sec. 7 or the most southwesterly center of Sec. 8, and thin sections made of this magnetic zone, more information could be obtained as to the true association of the magnetite to the dolomite. Unfortunately, no cores were obtainable in the area. Recently this area was purchased by the Farm Bureau of Lansing from the Swan-King Company of Mt. Pleasant, Michigan. Mr. Jack Mortensen, Consulting Geologist, Mt. Pleasant, Michigan, is now the geologist in charge of the Reynolds Field. It is my belief that Mr. Mortensen could be approached to obtain one core in this area from the top of the anhydrite for some distance down. It is recommended that a magnesium to calcium ratio be run on this core at one foot intervals to obtain a more complete relationship.

Because of the unusual occurrence of magnetite, it would also be deemed advisable to run a trace element survey on this same core to contribute more information to the study of dolomites in the Michigan Basin.

In massive limestone and dolomitic formations, insoluble residue studies have been run to correlate

depths of zones. Possibly this analytical method could be applied to the same insoluble residue zones to check the lateral distances that formations could be correlated by this method.

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