SIGNIFICANCE OF THE MAGNESIUM / CALCIUM RATIO AS RELATED TO STRUCTURE IN THE STONY LAKE OIL FIELD, MICHIGAN

Thesis for the Degree of M. S.
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This is to certify that the

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W. A. Kelly
Major professor

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SIGNIFICANCE OF THE MAGNESIUM/CALCIUM RATIO AS RELATED TO STRUCTURE IN THE STONY LAKE OIL FIELD, MICHIGAN

By

ROBERT THOMAS YOUNG

A THESIS

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ABSTRACT

The occurrence of secondary dolomite or dolomitic limestone adjacent to zones of weakness normally found in solid rocks has long been known to geologists. The development of tension fractures along the apices of folds, and the existence of other fractured zones related to structure, has also been observed. That dolomitization should occur along the zones of weakness related to structure is a natural conclusion. In order to test this hypothesis it was decided to analyze a series of samples from a dolomitized limestone formation in an area where a definite structure is present.

The Stony Lake Oil Field of Oceana County, Michigan, was selected as having the requisite qualities for such an investigation. Samples from this field were analyzed for calcium and magnesium content by titrating the prepared samples with versenate. This relatively new method gives rapid and accurate results, either on a percentage basis

or in the form of a ratio. Results of the analyses were expressed in terms of magnesium/calcium ratios. The ratios for various intervals were plotted on base maps of the field and contoured in the form of lithologic ratio maps. It was hoped that comparison of the ratio maps with the structural map of the field would show the existence of a definite relationship or pattern such as might be expected if dolomitization had occurred along zones of weakness developed in the formation because of folding. This, however, was not the case and it was concluded that, in the Stony Lake Oil Field, there was no recognizable relationship between the structure and the degree of dolomitization in the Traverse limestone as reflected by the magnesium/calcium ratios. Future work with other formations in other areas may yet establish the existence of such a relationship.

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INTRODUCTION

The occurrence of secondary dolomite or dolomitic limestone adjacent to zones of weakness has been noted by many authors. Geikie (1882, p. 305) early recognized such occurrences and attributed them to the action of circulating waters. Steidtman (1917, p. 448) in his work on the origin of dolomites states that secondary dolomites can be recognized by their relation to faults, fissures, and other secondary openings. Hatch, Rastall, and Black (1928, p. 193) discussed this phenomenon further:

> In the most characteristic occurrences, the secondary dolomite is clearly related to the planes of weakness normally found in solid rocks, the commonest channels of dolomitization being fault planes, joints, and minor fractures.

In Michigan and elsewhere 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. Although in two of the fields which he cited 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 structure, Landes felt that there might be more than an accidental relationship between the position of the dolomite body and the rock structure. In explaining the porosity that is confined to locally dolomitized zones in limestones 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 $MgCO_3$ content and indicated that its presence in more than average quantities might well be the basis for lateral exploration in the hope of finding true dolomite.

Jodry (1954, pp. 38 and 39) expressed the belief that dolomitization occurs on the apices of folded structures, as well as along faults and fissures, as the result of the action of ascending waters. His study of dolomitized zones in the Rogers City formation in central Michigan tends to bear out this belief. Application of the versenate method for determining calcium and magnesium in the Rogers City formation, and mapping of the Mg/Ca ratios thus obtained, resulted in a lithologic ratio map of the area which coincides closely with a subsurface structural contour map of the formation. A certain paucity of control, however, is indicated by the fact that in the four townships which were studied only 44 wells penetrated to the Rogers City formation. Even with the data available 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 Mg/Ca 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 Mg/Ca ratios, to the study of an area with well controlled structure from which plenty of samples would be available.

SELECTION OF AN AREA

Any area selected to demonstrate the relationship between subsurface structure and the degree of dolomitization as reflected by the Mg/Ca ratio must have the following attributes: (1) a locally dolomitized limestone formation must be present, (2) a structure of considerable magnitude should be reflected in this formation, (3) an abundance of control should be available for contouring the subsurface structure, and (4) good samples of the formation should be available, distributed as evenly as possible over the lateral and vertical extent of the structure.

A preliminary investigation to determine which areas might best fulfill these requirements was restricted to the oil and gas fields of Michigan. It was felt that these would not only afford the best possibilities in regard to control and samples, but would also, should a definite relationship be established between lithologic ratio maps of the Mg/Ca ratios and structure or porosity in dolomitized formations, be the object of major application of such a relationship.

Of the dozen fields judged most suitable from the standpoint of formation, size, structure, and structural control few met the test of sample availability. In several instances the samples had been destroyed. Development of some fields by numerous petroleum companies, large and small, made the possibility of obtaining samples questionable in several cases. Fortunately, excellent sample coverage of the Stony Lake Oil Field was available from the Carter Oil Company.

While not necessarily the best choice from all points of view, this field was selected as having the best combination of necessary properties for the purposes of this study.

THE STONY LAKE OIL FIELD

Location and extent. The Stony Lake field is located two to three miles southeast of the village of Benona, Claybanks Township (T13N-R18W), Oceana County, Michigan (see Figure 1.). The producing area, confined to sections 9, 10, 11, 14, 15, and 16, is well delineated and extends for about two miles northeast to southwest and one and a half miles northwest to southeast (see Figure 2.). The total drilled acreage is 1,540.

History of development. The Stony Lake pool was discovered in December, 1946 by the Carter Oil Company's #1 Martin Miller well, NE-SW-SW, section 11. Subsequent development of the field followed a 20-acre diagonal spacing pattern. To date there have been 85 wells drilled in or immediately adjacent to the producing area. Of these, 78 were producers and, as of the end of 1953, 71 wells were still in production. All dry holes were drilled on fringe locations. The field is almost entirely the property of the Carter Oil Company.

Production. During the first year of development the Carter Oil Company established a voluntary production rate of 100 barrels of oil per well per day. The State of Michigan has since established a proration of 50 barrels of oil per well per day or 100 barrels of oil per 40-acre unit per day. According to the Michigan Geological Survey (1953), cumulative production to the end of 1953 amounted to 5,402,697 barrels of oil of which 608,671 were produced during 1953. Production has been nearly the same for the last three years. Brine production during 1953 amounted to 4,456 barrels per day, almost all of which was handled by subsurface disposal methods. To the end of 1953 the average recovery of oil per acre drilled was 3,508 barrels.

Producing zones. All wells but one produce from the Traverse limestone of Devonian age. According to Carter geologists (1954, personal communication), two separate and distinct pay zones are encountered. The upper zone consists of thin, erretically developed streaks of porosity found in the first 0 to 10 feet of the Traverse limestone. The rock is characteristically a fairly dense, brown to tan limestone exhibiting scattered pinpoint to vugular porosity. No definite oil-water contact has been found and an effective water or gas drive is lacking. The lower producing zone is encountered 15 to 30 feet below the top of the Traverse limestone in a light gray, fossiliferous limestone exhibiting good vugular and primary coralline porosity. A definite oil-water contact is in evidence at an approximate subsea depth of -953 feet. Because of the uniform porosity development the lower producing zone is a good water-drive reservoir. About five-sixths of the wells produce from the lower zone, most of them flowing naturally.

Stratigraphy. It is generally agreed that the Traverse group includes that series of beds extending upward from the base of the Bell shale to the base of the Antrim formation. Some disagreement, however, has arisen as to the inclusion of the gray shales and thin beds of argillaceous limestone near the base of the Antrim formation. Cohee (1947) considered these to be the basal strata of the overlying Antrim formation. Hake and Maebius (1938, p. 457) excluded this zone from the Traverse group and recognized it only as a transition phase between the Traverse group and the brown to black shales of the Antrim formation. In western Michigan the zone consists of a series of gray shales with occasional limy beds resting on a characteristic limestone member of the Traverse group. Here it generally has been accepted by petroleum geologists as a member of that group and is referred to as the "Traverse formation". The underlying limestone, consisting of up to several hundred feet of limestone and dolomitic limestone, is commonly referred to as the Traverse limestone. These terms will be used in this study with the indicated connotations. Because of the distinct and easily recognized lithologic break between the Traverse limestone and the shales of the overlying "Traverse formation" the former is used as a contouring horizon by petroleum geologists and others. The structural contour map of the Stony Lake pool (Figure 4) is contoured on this horizon.

Several attempts have been made to divide the Traverse group into separate lithologic units and to correlate these units, where possible, across the Michigan basin. In one of the most recent articles dealing with the Traverse group Cohee (1947) states that the upper beds of the Traverse limestone of western Michigan are probably Thunder Bay in age. Figure 8 of his chart shows the southeastern part of Oceana County to be underlain by the Thunder Bay limestone and the rest of the county (including the Stony Lake field) to be underlain by the Squaw Bay limestone of younger age. Henry (1949, p. 8) divided the upper several hundred feet of the Traverse limestone into five separate lithologic units on the basis of an examination of samples and electric logs from wells in the Pentwater field of Mason and Oceana Counties. Due to lateral and basinward changes in lithology no attempt was made to correlate these units with previously established divisions of the Traverse. Henry mentions (1949, p. 2) that both the Pentwater and Stony Lake fields have been termed reef-like producing pools. Because of the location of the Pentwater field (about 18 miles north of Stony Lake field) his investigation is of special interest.

In the Stony Lake field the Traverse limestone (from the top downward) consists of 3 to 5 feet of brown, crystalline dolomite and dolomitic limestone with some pinpoint to vugular porosity; 5 to 15 feet of brown to tan, fairly dense limestone and dolomitic limestone with scattered pinpoint to vugular porosity; and a zone of undetermined thickness, the upper part of which consists of light gray fossiliferous and crystalline limestone with coralline and vugular porosity. Since few samples extended more than 25 feet below the top of the Traverse limestone a more extensive description from personal examination of the lithology is not available. For a generalized section of the Traverse group in the Stony Lake field see Figure 3.

Structure. The general structural configuration of the Stony Lake pool, as contoured on the top of the Traverse limestone (Figure 4), resembles a dome with nearly 100 feet of closure. Carter geologists (1954, personal communication) believe that the structure is the result of crossfolding with the major axis trending in a northwest-southeast direction and the minor axis in a northeast-southwest direction. If this is the case the structural alignment is in agreement with the general trends in western Michigan. The possibility of a reef structure has already been mentioned.

As a check on the nature of the structure of the Stony Lake pool, a structural plat was constructed using the top of the "Traverse formation" as the contouring horizon. When compared with the structural plat contructed on the top of

the Traverse limestone, the contours of the two were found to be nearly concentric with a difference of about 70 feet in the depths of corresponding contour lines. No flattened effect or drape folding was evident in the upper horizon, in fact a slight steepening was indicated on the extreme east and west flanks of the structure (in sections 8 and 12). If the major relief of the structure was due to a reef formation it seems likely that the structure as reflected in the overlying shale section would be considerably flattened. Since this is not the case it is considered that the structure is primarily of a tectonic nature and probably due to cross-folding in agreement with the general structural trend in the area. This does not obviate the possibility that a reef structure is present in the lower producing zone of the Stony Lake pool. Such a structure may have been of low relief or graded laterally into normal limestone thus presenting a nearly flat surface prior to the folding. Because the structure in the Traverse limestone is almost perfectly reflected in the overlying Coldwater formation of Mississippian age, the age of folding is considered to be post-Mississippian .

METHOD OF ANALYSIS

Until recently the methods available for the analysis of calcium and magnesium in limestones and dolomites involved either the time-consuming precipitation and separation of the two in solution, or staining of the sample with Lemberg's solution, silver chromate, or potassium ferricyanide. The latter methods often required the preparation of polished slabs or thin sections and, upon staining, careful and detailed examination was necessary to determine the amounts of calcite and dolomite present.

In Helvetica Chimica Acta for 1947 and 1948 Schwartzenbach and co-workers of the University of Zurich reported the results of a series of investigations of the complex ions of the alkaline-earth and other metals with aminopolycarboxylic acids, and suggested the use of ethylenediaminetetraacetic acid (commonly called versene) as a titrant for the sum of calcium and magnesium in water, using a dye, Eriochrome black T (F-241), as an indicator. This usage is based on the fact that both versene and F-241 form slightly ionized compounds with calcium and magnesium. One of the salts formed by the neutralization of versene with sodium hydroxide, disodium dihydrogen versenate, is used in preparing the titrating solution. As the titration progresses the versenate first combines with the free calcium ions, then with the free magnesium ions, and finally, at the end point, extracts the magnesium from the soluble, wine-red dye compound formed by magnesium and F-241. At this point the color changes sharply from wine-red to clear blue.

The versenate method for obtaining total calcium and magnesium has been successfully applied to the analysis of limestone by J. J. Banewicz and C. T. Kenner (1952, p. 1186) who used this method in analyzing 500 feet of core from an oil well. They, however, combined the versenate method with the calcium oxylate separation in order to obtain separate values for calcium and magnesium. In a later article Cheng, Kurtz, and Bray (1952, p. 1640) of the University of Illinois elaborated upon the use of the versenate method for determining total calcium and magnesium in limestones and supplemented it by describing a simple method of titrating for calcium alone by using ammonium purpurate (murexide) as an indicator with the versenate. Results obtained with the versenate titration in analyzing standard samples were in excellent agreement with results obtained by conventional procedures.

Since the versenate method has not yet been described in any of the publications generally available to geologists, it is outlined here in some detail, with such modifications as have been found convenient by the author. The techniques described by Cheng, Kurtz, and Bray were used as a guide.

Of special importance in the following procedures is the use of distilled water in the preparation of all aqueous solutions and in washing equipment.

Samples

Source. Carefully selected core chips or pieces of outcrop offer perhaps the best type of sample for analysis. Cable tool samples are usually satisfactory and unless the sample is very finely ground a representative portion can often be selected megascopically. Samples obtained with rotary tools (except cores) are difficult to work with for the following reasons: (1) the necessary quantity of sample is not often available in the first shows, (2) it is difficult to locate the sample correctly as to depth, and (3) separation of a suitable sample must often be made microscopically, at least from the earlier shows. If the stratigraphy, lithology, and drilling practices of an area are well known to the analyst foreign material in the samples is quite easily determined, either from empirical data or from the spasmodic occurrence of such material in the section.

Preparation. Samples must first be thoroughly washed and dried. Pieces of caving and other foreign material should be removed and a magnet passed through the sample to pick up any pieces of "junk" iron which may be present. If only a ratio of calcium and magnesium, instead of exact percentages, is desired, cherts and other relatively inert materials of a non-limy nature need not be separated from the sample. Crushing ofthe larger fragments will aid in rapid and complete digestion.

Quantity. Samples of 1.00 gram were recommended by Banewicz and Kenner (1952, p. 1186) and Cheng, Kurtz, and Bray (1952, p. 1640) as being of optimum size. Satisfactory results were obtained by the author with samples as small as 0.25 gram. Unless only small samples are available, however, it is recommended that, for convenience in handling and calculating, 0.50 gram or 1.00 gram samples be used throughout any one series of analyses.

Digestion. Weigh 1.00 gram of properly prepared sample into a 250-milliliter beaker and add 10 milliliters of hydrochloric acid (1 to 1)[1] and 15 milliliters of water (distilled). Evaporate to dryness, bake residue for a short time (10 to 30 minutes), and allow to cool. Take up residue by adding 3 milliliters of hydrochloric acid (1 to 1) and 10 milliliters of water. Filter the solution and make up to 250 milliliters with water (a 250-milliliter volumetric flask is convenient for this purpose).

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[1] Cheng, Kurtz, and Bray (1952) recommended the use of perchloric acid for digesting samples. Because of the dangerous fumes evolved hydrochloric acid was substituted and proved to be satisfactory.

Laboratory Equipment

The following equipment was utilized during the analyses:

Balance and weights
5-gallon carboy with siphon (for distilled water)
Mortar and pestle
50-milliliter burette (graduated)
250-milliliter beakers (2)[1]
100-milliliter beaker (1)[1]
200-milliliter porcelain dish (1)[1]
50-milliliter glass funnel (1)[1]
200-milliliter volumetric flask
1-liter graduate
50-milliliter graduate
10-milliliter volumetric pipette
5-milliliter volumetric pipette
Assorted tweezers, stirring rods, spatulas, etc.

In addition to the above equipment it was found convenient to have, besides the original large containers, small dropper bottles and a 0.10 gram measuring spoon from which to dispense the indicators and other reagents during titration. A large Erlenmeyer flask equipped with a spout of tubing was used to replenish the burette between titrations.

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[1] If samples are run in batches the quantity of equipment indicated in parentheses will be required for each sample in the batch.

All standard solutions, reagents, and indicators were kept tightly stoppered when not in use. Small quantities of solutions remaining in dispensing bottles after a series of determinations were thrown out and the supply replenished from the original containers. All pieces of equipment were washed in distilled water and the volumetric flasks and pipettes were rinsed after each usage.

Reagents and Solutions

Required for Calcium Determination

Versenate solution. Place 4.00 grams of disodium dihydrogen ethylenediaminetetraacetate dihydrate[1] in about 100 milliliters of distilled water and, when thoroughly dissolved, dilute to exactly 1 liter. Standardize this solution against the standard calcium and standard magnesium solutions as described hereafter.

Standard calcium solution. Dissolve 2.495 grams of calcium carbonate[2] in about 5 milliliters of hydrochloric acid (1 to 1) and dilute to 1 liter with water. This solution contains 1.000 milligram of calcium per milliliter.

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[1] Available from the Hach Chemical Company of Ames, Iowa as "TitraVer".

[2] Standard calcium solutions were prepared with both reagent grade calcium carbonate and Iceland spar. Identical results were obtained when the versenate solution was standardized against the two .

Potassium hydroxide. Prepare a 20 percent aqueous solution. This solution serves to adjust the pH value of the sample for titration.

Calcium indicator powder. Thoroughly mix powdered potassium sulfate and murexide in a ratio of 99 to 1. This item may be obtained in prepared form as "CalVer" from the Hach Chemical Company. Several mixtures of potassium sulfate and murexide were tried and the quantity of indicator powder used in successive determinations of a single sample was varied. Results were essentially the same but it was found that the best colors and color changes were obtained using approximately 0.10 gram of the 99 to 1 mixture.

Required for Magnesium Determination

Versenate solution. As previously described.

Standard magnesium solution. Dissolve 3.47 grams of reagent grade magnesium carbonate or 1.66 grams of magnesium oxide in 5 milliliters of hydrochloric acid (1 to 1) and dilute to 1 liter with distilled water. This solution contains 1 milligram of magnesium per milliliter.[1]

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[1] Standardization of the versenate solution with the original standard magnesium solutions prepared as above did not give results agreeable with those calculated from the molality of the versenate solution as found with the standard calcium solution. A new standard magnesium solution was prepared using magnesium oxide obtained by heating reagent grade magnesium carbonate to a temperature of 1500 degrees centigrade for several hours in an electric oven. Excellent correlation was achieved with this solution.

Buffer solution. Dissolve 67.5 grams of ammonium chloride and 5 grams of the magnesium salt of versenate[1] (obtainable from the Hach Chemical Company) in about 200 milliliters of water, add 570 milliliters of concentrated ammonium hydroxide, and dilute to 1 liter with water. This solution serves to adjust the pH of the sample being titrated to a suitable value (about 10).

Potassium cyanide. Prepare a 10 percent aqueous solution. The addition of this solution to the sample largely overcomes interference with the end point occasioned by the presence of iron, copper, cobalt, or nickel.

F-241 indicator. Dissolve 0.15 gram of Eriochrome black T (F-241, available from the Hach Chemical Company) and 0.50 gram of sodium borate in 25 milliliters of methanol. In solution this indicator was found to be stable for several weeks. Since the methanol evaporates readily, the container should be kept stoppered except when actually dispensing the indicator.

Quantities Required

The following quantities of material were necessary to prepare and make a complete calcium and magnesium deter-

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[1] The addition of the magnesium salt of versenate is necessitated by recent refinements in the versenate obtainable (Hach, 1954, personal communication).

mination for one sample. The figures are based on the use of a 1.00 gram sample made up to 250 milliliters in solution, of which a 10 milliliter aliquot was tested.

Distilled water	310 milliliters
Hydrochloric acid (1 to 1)	13 milliliters
Filter paper (number 1)	1 each
Versenate solution	74 milliliters[1]
Potassium hydroxide solution	1 milliliter
Calcium indicator powder	0.10 gram
Buffer solution	2 milliliters
Potassium cyanide solution	0.10 milliliter
F-241 indicator	0.40 milliliter

These figures are given as a guide in estimating the quantities of the various materials which might be required for a series of analyses. Plenty of additional distilled water should be available for washing equipment and an extra 20 percent of all material should be allowed to cover standardizing, re-titrations, and similar items.

Standardization of Versenate Solution

With standard calcium solution. Take a 10 milliliter aliquot of the standard solution and proceed as described for the titration of calcium, using murexide as the indicator.

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[1] Average quantity required for calcium and total calcium and magnesium determinations per sample. Based on average for 20 samples.

With standard magnesium solution. Take a 10 milliliter aliquot of the standard solution and proceed as described for the titration of total calcium and magnesium, using F-241 as the indicator.

Titration

For calcium. Pipette a 10 milliliter aliquot of the solution to be analyzed into a 200-milliliter porcelain dish, then add about 20 milliliters of water, 1 milliliter of potassium hydroxide solution, and approximately 0.10 gram of calcium indicator powder. Stir, and titrate with the standardized versenate solution. The end point is reached when the color changes from pink to violet. The sample should be titrated immediately after the addition of the calcium indicator powder as the latter is not stable in solution. A series of determinations of the same sample was made immediately following the addition of the indicator powder and ten, twenty, and forty minutes later. Negative errors of up to 12 percent were noted in the delayed determinations.

For total calcium and magnesium. Pipette a 10 milliliter aliquot of the solution to be analyzed into a 100-milliliter beaker, then add about 25 milliliters of water, 2 milliliters of buffer solution, several drops of potassium cyanide solution, and 8 drops of F-241 indicator. Stir, and titrate with the standardized versenate solution. The end point is reached when the color changes from wine-red to clear blue. Care should be taken to add the reagents in the order indicated. If the indicator is added before the buffer solution or potassium cyanide solution, interference by iron is likely to be encountered. This will give a pink tinge to the blue color beyond the end point. A series of determinations of the same sample, made immediately after, and at ten, twenty, and forty minutes following, the addition of the indicator, gave identical results. For convenience and speed in carrying out the determinations it is recommended that the titration for calcium be made first. It is then possible to add swiftly at least the same amount of versenate solution to the sample when titrating for total calcium and magnesium.

Color Standards

Since the colors involved in the titrations are not stable for more than a short time it is not possible to establish permanent comparative color standards. Furthermore, the end point obtained with the calcium indicator powder (pink to violet) is not as sharp as that obtained with the F-241 indicator (wine-red to blue). In order to check the end point obtained with the calcium indicator, titrations of the standard calcium solution were made with both the calcium indicator and F-241. The sharp end point obtained with the latter was used as a reference

when titrating with the calcium indicator and, with a little practice, it was possible to obtain excellent agreement between the two end points.

Calculations

For Standardizing Versenate Solution

With standard calcium solution. 25.2 milliliters of versenate solution were required to titrate, to the end point, 10 milliliters of the standard calcium solution. Since this solution contained 1.00 milligram of calcium per milliliter, 0.397 milligram of calcium was titrated by each milliliter of versenate solution (10/25.2 = 0.397).

With standard magnesium solution. 41.3 milliliters of versenate solution were required to titrate, to the end point, 10 milliliters of the standard magnesium solution. Since this solution contained 1.00 milligram of magnesium per milliliter, 0.242 milligram of magnesium was titrated by each milliliter of versenate solution. As a check the milligrams of magnesium per milliliter of versenate solution were calculated from the results obtained with the standard calcium solution as follows:

$$\frac{\text{Atomic weight of magnesium}}{\text{Atomic weight of calcium}} = \frac{24.32}{40.08} = 0.607$$

$$0.607 \times 0.397 = 0.241$$

This calculated value agrees closely with that obtained using the standard magnesium solution. Since any impurities present in the magnesium compound used in preparing the standard solution would have the effect of raising the figure, the calculated value (0.241, the lower of the two) was accepted as being most nearly correct.

Calculations for successive batches. Eight separate batches of versenate solution were prepared and standardized with the standard calcium and magnesium solutions. The results were essentially the same with each batch and the original calculations were thus validated for the entire series of analyses.

Calculations for Calcium and Magnesium

Given:

A = milligrams of calcium per milliliter of versenate solution.

B = milliliters of versenate solution used in titration with murexide as indicator (for calcium).

C = milligrams of magnesium per milliliter of versenate solution.

D = milliliters of versenate solution used in titration with F-241 as indicator (for total calcium and magnesium.

Then the quantities of calcium and magnesium present in the sample can be calculated as follows:

$$\text{Calcium} = \frac{A \times B}{(\text{Weight of sample titrated})}$$

$$\text{Magnesium} = \frac{C \times (D - B)}{(\text{Weight of sample titrated})}$$

If a 1.00 gram sample is made up to a 250 milliliter solution and a 10 milliliter aliquot is taken for titration, the percentages of calcium and magnesium can be calculated as follows:

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

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

Ratios

Selection. On a molecular basis the ratio of calcium to magnesium varies from 1.000 in a normal dolomite ($CaMg(CO_3)_2$) to infinity in a pure limestone ($CaCO_3$) while the magnesium/calcium ratio varies from 1.000 to zero. Since the results of much recent quantitative work have been expressed in terms of weight it was thought desirable to express the ratios used herein on that basis. The ratio of calcium to magnesium thus will vary from 1.644 (in a normal dolomite) to infinity (in a pure limestone) and the magnesium/calcium ratio will vary from 0.607 to zero. Obviously, the use of the magnesium/calcium ratio on either basis will give results within well defined limits which can easily be applied to the construction of charts, graphs, and maps regardless of the relative quantities of calcium and magnesium present.

<u>Calculations</u>. The ratio of magnesium to calcium can be calculated from the relative percentages of each as previously determined. A more direct method of calculating the ratio is as follows:

$$\frac{\%\ \mathrm{Mg}}{\%\ \mathrm{Ca}} = \frac{C \times (D - B) \times 2.5}{A \times B \times 2.5} = \frac{C(D - B)}{AB}$$

Since C and A bear a constant relationship to each other as determined by the respective atomic weights of magnesium and calcium, the ratio can be even more simply expressed. Thus:

$$\frac{\mathrm{Mg}}{\mathrm{Ca}} = 0.607 \times \frac{D - B}{B}$$

To obtain the magnesium/calcium ratio with this formula neither the weight of the sample nor the strength of the versenate solution is required. The formula thus lends itself readily to use in mass analyses or field work where the ratio alone is sufficient.

TABLE I

WELL AND SAMPLE DATA

Permit #	Well Name[1]	Location	Top of "Traverse Formation"	Top of Traverse Limestone
12742	#1 M. H. Miller	NE-SW-SW-11	-845	-913
13024	#1 Schiller Unit	NE-NE-NE-15	-850	-910
13077	#1 J. Schiller	NE-NE-SE-10	-839	-910
13096	#1 E. Eilers	NE-NW-NE-15	X[2]	-896
13106	#1 L. Eilers	NE-SE-SE-10	X	-906
13148	#1 K. Schiller	NE-SW-SE-10	-837	-897
13180	#1 H. Weber (ROWMER CORPORATION)	SE-SW-NE-8	-918	-984
13191	#1 E. Hoffman	NE-SW-NE-15		

[1] Unless otherwise noted all wells belong to the Carter Oil Company and are named on that basis.

[2] The symbol "X" is used where information is unavailable or highly questionable.

TABLE I (Continued)

WELL AND SAMPLE DATA

Sample Interval Below Traverse Limestone	Per-cent Mg	Per-cent Ca	Mg/Ca Ratio	Mg/Ca Ratio for Indicated Interval[1]			
				0-2½	0-5	0-10	5-10
0-4	2.0	23.5	0.087	X	X	X	X
4-7	1.0	21.7	0.044				
7-16	0.6	35.8	0.017				
16-22	0.8	38.2	0.022				
22-24	0.8	39.1	0.021				
0-3	2.8	29.8	0.093	0.093	0.111	0.100	0.091
3-5	3.4	24.3	0.138				
5-11	2.6	29.0	0.091				
11-20	1.3	34.0	0.039				
20-24	1.9	34.0	0.057				
0-2	10.4	19.1	0.545	0.545	X	0.164	X
2-11	2.8	35.0	0.079				
3-6	8.0	24.7	0.325	X	X	X	0.096
6-9	3.7	30.0	0.124				
9-11	1.9	36.2	0.053				
11-16	2.5	35.4	0.071				
0-3	3.1	21.6	0.145	0.145	X	X	X
3-7	4.6	24.9	0.184				
7-16	2.3	34.0	0.067				
0-3	11.8	23.3	0.505	0.505	0.315	X	X
3-6	3.9	30.8	0.125				
0-6	9.7	21.6	0.452	X	0.452	X	X
0-2	8.5	15.6	0.547	0.547	X	X	X

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[1] Intervals are generalized. For complete explanation see text under "Consideration of Data - Selection of intervals to be mapped".

TABLE I (Continued)

Permit #	Well Name	Location	Top of "Traverse Formation"	Top of Traverse Limestone
13197	#2 J. F. Miller	NE-NE-SW-11	-857	-928
13243	#2 E. Eilers	NE-SE-NW-15	X	-906
13267	#1 Fulljames et al (NEIL WAGENAAR)	NW-SE-SW-12	-924	-976
13286	#1 L. Stevens	NE-SW-NW-15	-829	-901
13334	#1 R. Schiller	NE-NE-SW-10	-832-	-909
13348	#1 V. Schiller	NE-SW-SW-10	X	-899
13419	#1 J. V. Schiller	NE-NW-SE-10	-837	-904
13445	#1 S. J. Schiller	NE-SE-SE-9	-836	-907
13499	#1 W. Miller	NE-SE-NE-16	-846	-911
13500	#1 E. Friday	NE-NW-SW-10	-841	-909
13530	#2 S. J. Schiller	NE-NE-SE-9	-858	-929
13550	#3 S. J. Schiller	NE-SW-SE-9	-853	-923
13567	#1 M. B. Hunt	NE-NW-NE-16	-853	-922
13622	#3 E. Eilers	NE-NE-SW-15	-850	-929

TABLE I (Continued)

Sample Interval Below Traverse Limestone	Per-cent Mg	Per-cent Ca	Mg/Ca Ratio	Mg/Ca Ratio for Indicated Interval			
				0-2½	0-5	0-10	5-10
0-2	11.5	22.2	0.521	0.521	X	X	X
0-3	2.3	33.4	0.066	0.066	X	X	X
0-5	5.5	31.4	0.177	X	0.177	0.197	0.217
5-10	6.5	29.8	0.217				
0-10	2.4	35.2	0.068	X	X	0.068	X
10-15	0.7	38.9	0.019				
0-5	11.2	21.8	0.515	X	0.515	X	X
0-4	8.4	24.5	0.343	X	X	0.163	X
4-11	1.7	28.0	0.060				
0-6	12.2	20.4	0.596	X	0.596	0.359	0.074
6-11	2.7	35.8	0.074				
0-3	11.0	22.2	0.494	0.494	X	0.197	X
3-10	2.3	32.8	0.070				
0-4	4.8	29.4	0.164	X	X	X	X
0-4	11.3	20.2	0.560	X	X	0.298	X
4-9	4.5	32.2	0.139				
9-10	1.6	34.8	0.045				
0-6	12.1	20.2	0.595	X	0.595	X	X
6-15	0.8	38.7	0.022				
0-3	12.1	20.6	0.587	0.587	X	X	X
0-2	5.2	28.4	0.182	0.182	X	X	X
0-5	7.9	9.5	0.419	X	0.419	0.254	0.161
5-11	4.2	26.6	0.161				
11-16	1.4	35.8	0.041				

TABLE I (Continued)

Permit #	Well Name	Location	Top of "Traverse Formation"	Top of Traverse Limestone
13644	#1 S. Jacob	NE-SE-NE-10	-863	-934
13703	#1 M. Miller	NE-SW-NE-16	-860	-925
13723	#1 A. Schiller	NE-SE-NE-15	-869	-934
14138	#1 G. Schmiedeknecht	NE-NE-SE-16	-857	-933
14328	#1 R. O. Hamill	SE-NW-SE-9	-862	-929
14502	#1 State-Claybanks (MERCER OIL COMPANY)	NE-SE-NW-16	-868	-942
15065	#1 C. Eilers	SW-SE-NW-10	X	-918
15110	#4 S. J. Schiller	SW-NE-SE-9	X	-921
15190	#2 S. Jacob	SW-SE-NE-10	X	-919
15191	#3 J. F. Miller	SW-SW-NW-11	X	-927
15235	#4 J. F. Miller	SW-NW-SW-11	X	-909

TABLE I (Continued)

Sample Interval Below Traverse Limestone	Per-cent	Per-cent	Mg/Ca Ratio	Mg/Ca Ratio for Indicated Interval			
				0-2½	0-5	0-10	5-10
0-5	7.4	21.0	0.350	X	0.350	X	X
5-9	2.3	30.8	0.074				
9-14	0.7	38.7	0.019				
14-16	1.0	37.6	0.026				
0-5	12.5	22.1	0.567	X	0.567	0.321	0.116
5-9	4.4	34.2	0.130				
9-11	2.8	31.6	0.087				
11-18	0.6	38.0	0.016				
18-21	1.2	38.6	0.031				
0-5	6.5	21.2	0.307	X	0.307	0.263	0.219
5-10	6.4	29.2	0.219				
10-14	1.3	31.8	0.042				
14-18	1.0	33.8	0.029				
1-4	6.7	19.9	0.334	X	X	X	X
0-4	5.4	22.4	0.242	X	X	X	X
0-1	5.4	19.5	0.279	X	0.253	0.172	0.049
1-6	7.0	28.6	0.248				
6-10	1.8	37.0	0.049				
10-15	1.0	38.6	0.025				
0-3	2.9	34.6	0.084	0.084	X	0.082	X
3-10	2.4	29.8	0.081				
0-5	4.2	28.4	0.149	X	0.149	X	X
0-3	3.9	9.1	0.423	0.423	0.333	X	X
3-6	5.3	21.8	0.243				
0-2½	7.1	20.8	0.342	0.342	X	0.328	X
2½-9	7.5	21.3	0.346				
9-11	6.0	23.8	0.253				
0-2	2.7	22.4	0.109	0.109	X	0.164	X
2-8	4.6	26.2	0.175				
8-11	3.3	18.1	0.180				

TABLE I (Continued)

Permit #	Well Name	Location	Top of "Traverse Formation"	Top of Traverse Limestone
15256	#2 E. Friday	SW-NW-SW-10	X	-906
15275	#3 M. H. Miller	SW-SW-SW-11	X	-916
15351	#2 J. Schiller	SW-NE-SE-10	X	-905
15359	#3 L. Stevens	SW-SW-NW-15	X	-911
15415	#2 E. Blohm	SW-NE-NE-16	X	-912
15471	#4 M. Schiller	SW-SE-SW-10	X	-898
15494	#2 K. Schiller	SW-SW-SE-10	X	-888
15527	#5 E. Eilers	SW-NW-NE-15	X	-902
15570	#2 C. Eilers	NE-SE-NW-10	X	-928
15593	#1 W. Nichols (R. T. JONES)	SW-NE-NE-10	-886	-949
15626	#1 J. E. & A. M. Eilers	SW-NW-NW-11	-868	-954
15666	#1 Jonseek-Schiller	SW-SW-NE-10	X	-909

TABLE I (Continued)

Sample Interval Below Traverse Limestone	Per-cent Mg	Per-cent Ca	Mg/Ca Ratio	Mg/Ca Ratio for Indicated Interval			
				0-2½	0-5	0-10	5-10
0-6	6.4	20.2	0.316	X	0.316	0.239	0.114
6-10½	3.3	28.6	0.114				
0-2	1.9	25.4	0.076	0.076	X	X	X
0-2	7.6	20.2	0.375	0.375	X	0.258	X
2-10	5.5	24.2	0.229				
0-8	7.2	22.0	0.328	X	X	0.332	X
8-10	6.3	18.0	0.347				
1½-3	4.9	24.6	0.202	X	X	X	0.045
3-6	2.3	33.2	0.069				
6-9	2.0	30.8	0.067				
9-11	0.5	38.0	0.013				
1-4	11.8	21.4	0.550	X	X	0.255	X
4-11	3.6	28.0	0.129				
1-4	9.4	21.9	0.426	X	X	X	X
4-9	2.0	33.8	0.060				
9-15	0.6	39.9	0.015				
15-21	1.0	40.1	0.024				
0-3	5.9	21.6	0.272	0.272	X	X	X
0-5½	11.7	20.6	0.567	X	0.567	X	X
0-2	3.9	31.2	0.124	0.124	0.162	X	X
2-5	5.7	28.4	0.199				
0-1	10.1	20.0	0.506	X	0.457	X	X
1-5	8.0	17.9	0.445				
5-9	6.0	23.4	0.258				
9-15	4.8	27.2	0.177				
1-5	1.6	36.6	0.043	X	0.043	X	X

TABLE I (Continued)

Permit #	Well Name	Location	Top of "Traverse Formation"	Top of Traverse Limestone
15667	#2 Jonseek-Schiller	NE-SW-NE-10	X	-934
15683	#1 F. Osborn	NW-NW-SE-15	-855	-924
15689	#2 R. O. Hamill	NE-NW-SE-9	-874	-945
15751	#1 Kelley (OIL PRODUCERS)	NE-NE-NW-22	-900	-970
15799	#6 S. J. Schiller	SW-SW-SE-9	X	-936
15805	#4 M. H. Miller	SW-NW-NW-14	-864	-935
15890	#5 J. F. Miller	SW-NE-SW-11	-846	-912
15935	#1 Esther Friday	NE-SE-SW-9	X	-947
16059	#2 W. Miller	SW-SE-NE-16	-861	-931
16146	#2 M. B. Hunt	SW-NW-NE-16	-859	-926
16147	#1 H. P. Schneider	SW-SW-NE-9	-890	-957

TABLE I (Continued)

Sample Interval Below Traverse Limestone	Per-cent Mg	Per-cent Ca	Mg/Ca Ratio	Mg/Ca Ratio for Indicated Interval			
				0-2½	0-5	0-10	5-10
0-6	5.5	28.8	0.192	X	0.192	0.235	0.239
6-8	8.1	26.8	0.301				
8-11	5.9	30.0	0.197				
11-13	1.1	36.8	0.030				
13-14	1.8	24.8	0.073				
14-15	1.3	35.0	0.038				
1-6	4.3	29.0	0.149	X	0.149	0.115	0.081
6-11	2.8	34.2	0.081				
0-2	6.8	25.0	0.270	0.270	X	X	X
0-2	6.6	20.2	0.328	0.328	X	X	X
0-5	8.8	24.6	0.358	X	0.358	X	X
0-6½	4.3	27.0	0.161	X	X	0.146	X
6½-9	3.6	25.4	0.142				
9-11	2.6	26.4	0.100				
11-15	1.7	34.8	0.049				
0-1	8.8	22.4	0.389	X	0.308	X	X
1-5	7.6	26.4	0.288				
0-3	9.3	23.8	0.390	0.390	X	X	X
0-6	4.7	26.8	0.175	X	0.175	0.127	0.070
6-11	2.4	34.6	0.070				
0-2	11.3	22.2	0.510	0.510	0.300	0.186	0.013
2-6	5.7	29.0	0.195				
6-10	0.5	37.8	0.013				
10-15	0.5	37.8	0.013				
0-3	10.1	25.2	0.402	0.402	0.456	0.363	0.270
3-5	11.0	20.4	0.536				
5-7	11.7	22.2	0.526				
7-10	3.4	34.1	0.099				

TABLE I (Continued)

Permit #	Well Name	Location	Top of "Traverse Formation"	Top of Traverse Limestone
16485	#5 M. H. Miller	SW-SE-SW-11	-860	-927
16620	#2 A. Schiller	SW-SE-NE-15	-863	-934

TABLE I (Continued)

Sample Interval Below Traverse Limestone	Per-cent	Per-cent	Mg/Ca Ratio	Mg/Ca Ratio for Indicated Interval			
				0-2½	0-5	0-10	5-10
0-1½	3.7	30.6	0.122	X	0.065	X	X
1½-5½	1.6	36.7	0.043				
0-1	3.9	27.8	0.139	X	X	0.038	X
1-4	1.2	37.7	0.032				
4-7	0.8	38.3	0.022				
7-10	1.0	37.9	0.025				

CONSIDERATION OF DATA

Selection of intervals to be mapped. Preliminary analyses of samples from several wells located across the structure indicated that very little dolomitization had occurred at depths of more than 12 feet below the top of the Traverse limestone. Highest ratio values were confined to the top few feet.

A chart was prepared which showed sample intervals below the top of the Traverse limestone in the various wells. Distribution of the sample intervals was noted to be high at depths of about 5, 10, and 15 feet. In order to have as much control as possible for mapping, and to show the degree of dolomitization in the upper few feet of the formation, the following sample intervals were selected (given in feet below the top of the Traverse limestone):

0 to -2 or -3 (Figure 5.)
0 or -1 to -5 or -6 (Figure 6.)
0 or -1 to -10 or -11 (Figure 7.)
-5 or -6 to -10 or -11 (Figure 8.)
0 or -1 to -15 or -16
-10 or -11 to -15 or -16

Ratios for these intervals were calculated from the results of the analyses of the well samples. These were plotted areally on base maps of the Stony Lake field and the respective values were utilized in constructing a series of lithologic ratio maps. Although ratio maps were constructed for the last two intervals listed, control was so lacking and results so anomalous that inclusion of these maps was considered superfluous. The lateral extent of dolomitization of the different intervals can be seen by examination of the map of a particular interval and the degree of vertical dolomitization can be seen in part, by comparison of the maps of the different intervals. Comparison of the various lithologic maps to a subsurface structural contour map of the field (Figure 4.) should indicate whether or not there is any positive relationship between the degree of dolomitization, as reflected by the Mg/Ca ratios, and the structure.

<u>Vertical extent of dolomitization</u>. Mg/Ca ratios of the samples tested ranged from 0.013 to 0.596. The general pattern of vertical distribution within the Traverse limestone seemed to be from a high value in the upper 5 or 6 feet to a low value at a depth of about 13 feet and then a very slight increase in the ratio below that depth. Some rather low ratios were noted in the top few feet of the formation and in nine of these instances a slight increase in the

ratio was observed in the second sample. In four cases this increase may have been due to the inclusion of some of the overlying shale in the finely ground top samples. Previously, several analyses had shown this shale to be somewhat limy with an average Mg/Ca ratio of 0.083. In the other five instances the samples were free of shale, and lower ratios in the top samples may have been due to failure to get a representative sample. The possibility also exists that the extreme upper part of the formation may not have been as heavily dolomitized in places as a zone slightly below the top.

Inspection of the lithologic ratio maps revealed the following information:

#	Sample Interval (in feet below top of Traverse ls.)	Average Mg/Ca Ratio	Range of Mg/Ca Ratio
1	0 to -2 or -3	0.321	0.066 to 0.587
2	0 or -1 to -5 or -6	0.321	0.043 to 0.596
3	0 or -1 to -10 or -11	0.208	0.038 to 0.363
4	0 or -1 to -15 or -16	0.145	0.040 to 0.292
5	-5 or -6 to -10 or -11	0.124	0.013 to 0.270
6	-10 or -11 to -15 or -16	0.046	0.013 to 0.111

TABLE II

The similarity in ratios between intervals 1 and 2 would seem to indicate that the first six feet of the formation were dolomitized equally throughout. Comparison of successive values obtained for small sample intervals near the top of the formation, however, showed that a steady decrease in the ratio often can be expected from the top downward. Similarity of the two ratios may be due to the occasional presence of a less heavily dolomitized zone at the very top of the formation. The decrease in the average ratios at successively lower intervals, as illustrated by intervals 2, 5, and 6 (Table II), indicates that dolomitization decreases with depth, rather sharply at first and then more slowly. Inspection of values obtained from samples of individual wells showed this to be generally true with a very small increase in the ratio occurring below depths of about 13 feet in some wells. The decrease in the ratios shown in intervals 2, 3, and 4 also indicates a decrease in dolomitization or magnesium content with depth. The flattening effect of the overlapping intervals is apparent when compared to ratios obtained for intervals 2, 5, and 6.

Dolomitization in producing zones. Samples through the producing zones were available from some wells. Analyses of six of these wells did not reveal any significant change in the Mg/Ca ratio in these samples. Both high and low ratios were encountered depending largely on the depth of the producing zones below the top of the formation.

Lateral extent of dolomitization. Examination of the lithologic ratio maps and individual well analyses indicates that some dolomitization was present across most of the Stony Lake pool. The presence of both high and low ratios distributed over the field would further indicate that the degree of dolomitization or quantity of magnesium present varied considerably and that development of the dolomitized zones was rather irregular. Dry holes located on the flanks of the pool in sections 8, 12, and 22 did not have Mg/Ca ratios significantly different from those obtained in wells nearer the center of the pool.

RELATIONSHIP OF DOLOMITIZATION TO STRUCTURE

If the assumption holds true that dolomitization occurs along tension fractures developed on the apices of folds, a comparison of the lithologic ratio maps and the structural contour map of the Traverse limestone in the Stony Lake pool should show the existance of a definite relationship or pattern.

To this end the various lithologic ratio maps were contoured in several patterns. In order to develop any possible relationship each map was contoured individually several times. An attempt was also made to develop patterns which would be common to all ratio maps. Where control was lacking the Mg/Ca ratios of intermediate sample intervals were used as guides. Because most dolomitization apparently occurred in the upper six feet of the formation and because of the greater control available, emphasis was placed on ratio maps of the upper part of the formation. The ratio contours as shown in Figures 5, 6, 7, and 8 represent but a few of many possible interpretations.

The subsurface structural contour map of the Traverse limestone was constructed from data secured from the Michigan Geological Survey and the Carter Oil Company. In several cases of conflicting data the samples were checked and those values taken which best coincided with the lithologic change from shale to limestone. The density of control and logical pattern left little necessity for questionable contouring of the structure.

Direct comparison of the lithologic ratio maps and the structural contour map failed to disclose the existence of any recognizable relationship or pattern between them. Examination of the individual well analyses also failed to establish any definite relationship between the structure and the lateral or vertical extent of dolomitization. No recognizable pattern such as might be expected in the case of cross-folding, folding, or doming was apparent in any reasonable interpretation of the lithologic ratio maps.

ORIGIN OF DOLOMITE IN THE STONY LAKE FIELD

Several possibilities exist as to the origin of the dolomite near the top of the Traverse limestone. Although none of the individual well analyses showed a significant increase in, or sustained high value for, the Mg/Ca ratio at depths down to 24 feet, it is entirely possible that a number of irregularly spaced fractures extend down into the formation and that, at one time, magnesium-bearing waters circulated through these fractures from below. The relatively impervious beds of overlying shale would, in this case, tend to direct the waters laterally at the contact with the limestone. Interruption or discontinuance of the circulation could account for the irregular pattern of dolomitization. Because of the age (post-Mississippian) assigned to the folding, it seems unlikely that dolomitization could be due to the circulation of ground waters through tension fractures developed as a result of uplift and exposure following the folding.

If unrelated to fracturing developed during folding, the dolomitization might be due to the replacement of limestone beneath warm, shallow seas or lakes sometime after partial lithification of the limestone. The circulation of magnesium-bearing sea waters through borings or openings due to marine vegetation might then account for the irregular distribution of the dolomitized areas. Occasional recession of the unstable seas and subsequent non-deposition is also a possibility. It is not improbable that the Traverse limestone underwent uplift without appreciable folding on one or more occasions. In such a situation the dolomite could be due to dolomitization of the limestone by downward circulating groundwaters or to leaching of calcium from a dolomitic limestone. In the latter case subsequent compaction and re-dissolution and replacement may have served to impart to the dolomitized zone its present relatively non-porous condition.

CONCLUSIONS

The versenate method for determining calcium and magnesium in limestones and dolomites has proved to be rapid, simple, and accurate. The preparation of lithologic ratio maps based on Mg/Ca ratios appears to be a simple and logical way of presenting information obtained by applying the versenate method to analyzing a series of samples from a dolomitized zone in a particular area.

Although comparison of structural and ratio maps of the Traverse limestone in the Stony Lake pool did not reveal any significant relationship between the structure and the degree of dolomitization as indicated by the Mg/Ca ratio, the possibility of such a relationship existing in other formations and in other areas is not precluded. Only after extensive comparison of many structures and formations by means of structural and lithologic ratio maps can the value of this method of locating structural features and dolomitized zones be evaluated. The combination of the versenate method for determining calcium and magnesium and mapping of the results as a Mg/Ca ratio may yet prove to be a useful tool for the geologist.

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FIGURE 1.

INDEX MAP OF

STONY LAKE OIL FIELD

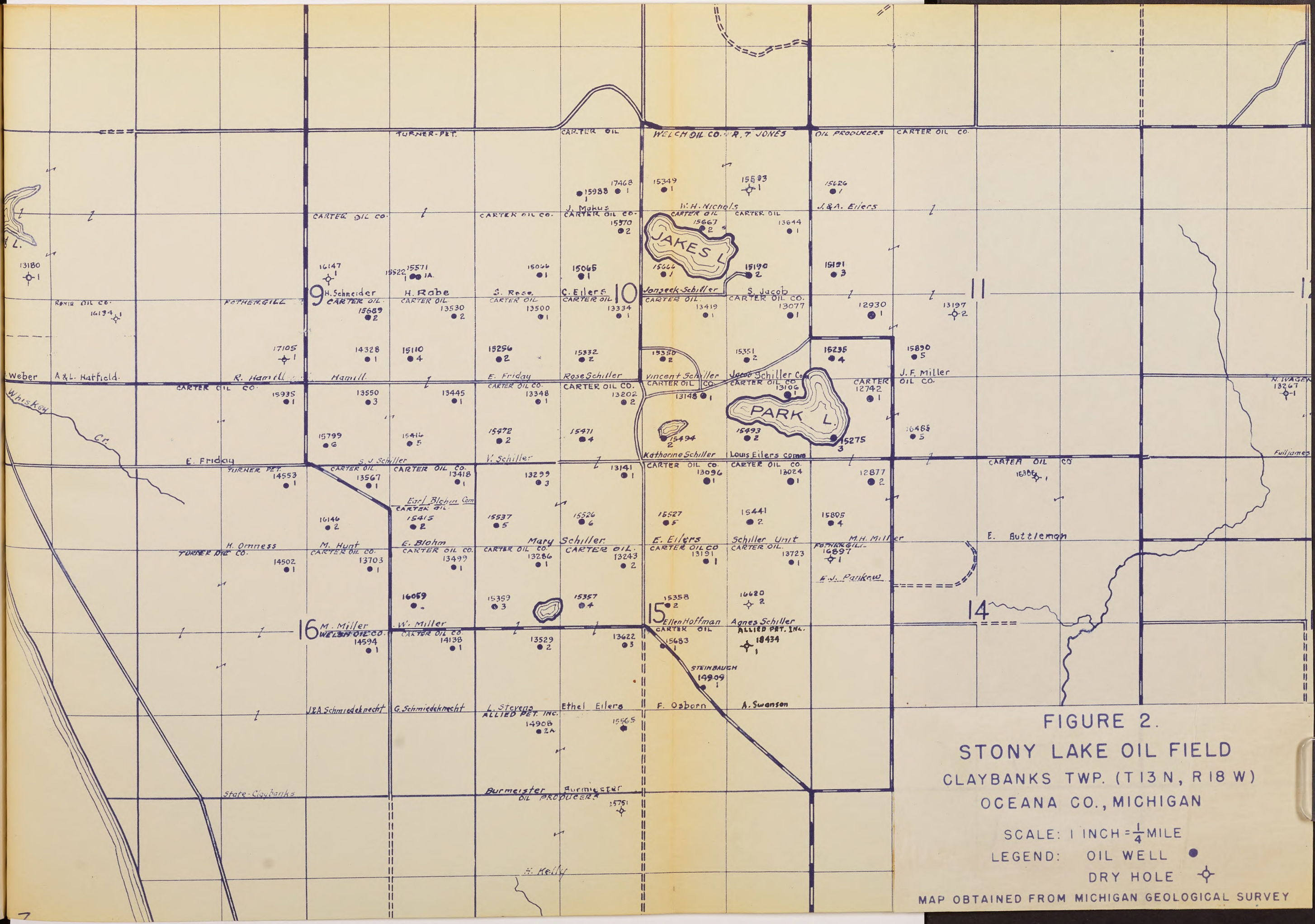

FIGURE 2.

STONY LAKE OIL FIELD

CLAYBANKS TWP. (T 13 N, R 18 W)
OCEANA CO., MICHIGAN

SCALE: 1 INCH = $\frac{1}{4}$ MILE

LEGEND: OIL WELL ●
DRY HOLE ⌖

MAP OBTAINED FROM MICHIGAN GEOLOGICAL SURVEY

SYSTEM	GROUP	FORMATION, MEMBER, OR STAGE	THICKNESS (FEET)	LITHOLOGIC DESCRIPTION
MISS DEV		Antrim Shale	210	Brown to dark brown shale
DEVONIAN		"Traverse Formation"	15	Light gray, crystalline limestone
			60	Gray shale w/ streaks of gray limestone
	TRAVERSE GROUP	Traverse Limestone	4	Brown, crystalline dolomite
			15	Brown to tan limestone & dolomitic limestone
			30	Tan to light gray, fossiliferous and/or crystalline limestone w/ vugular and coralline porosity
			190	Light gray, crystalline limestone
			10	Brown, dolomitic limestone w/ anhydrite
			35	Anhydrite and dolomite
			15	Sucrosic dolomite
			15	Sucrosic dolomite and anhydrite
			80	Sucrosic dolomite
		Bell Shale	40	Gray shale
		Dundee Limestone	50	Light brown, crystalline to granular limestone

FIGURE 3.
GENERALIZED STRATIGRAPHIC SECTION OF THE
TRAVERSE GROUP IN THE STONY LAKE OIL FIELD
SCALE: 1 INCH = 100 FEET

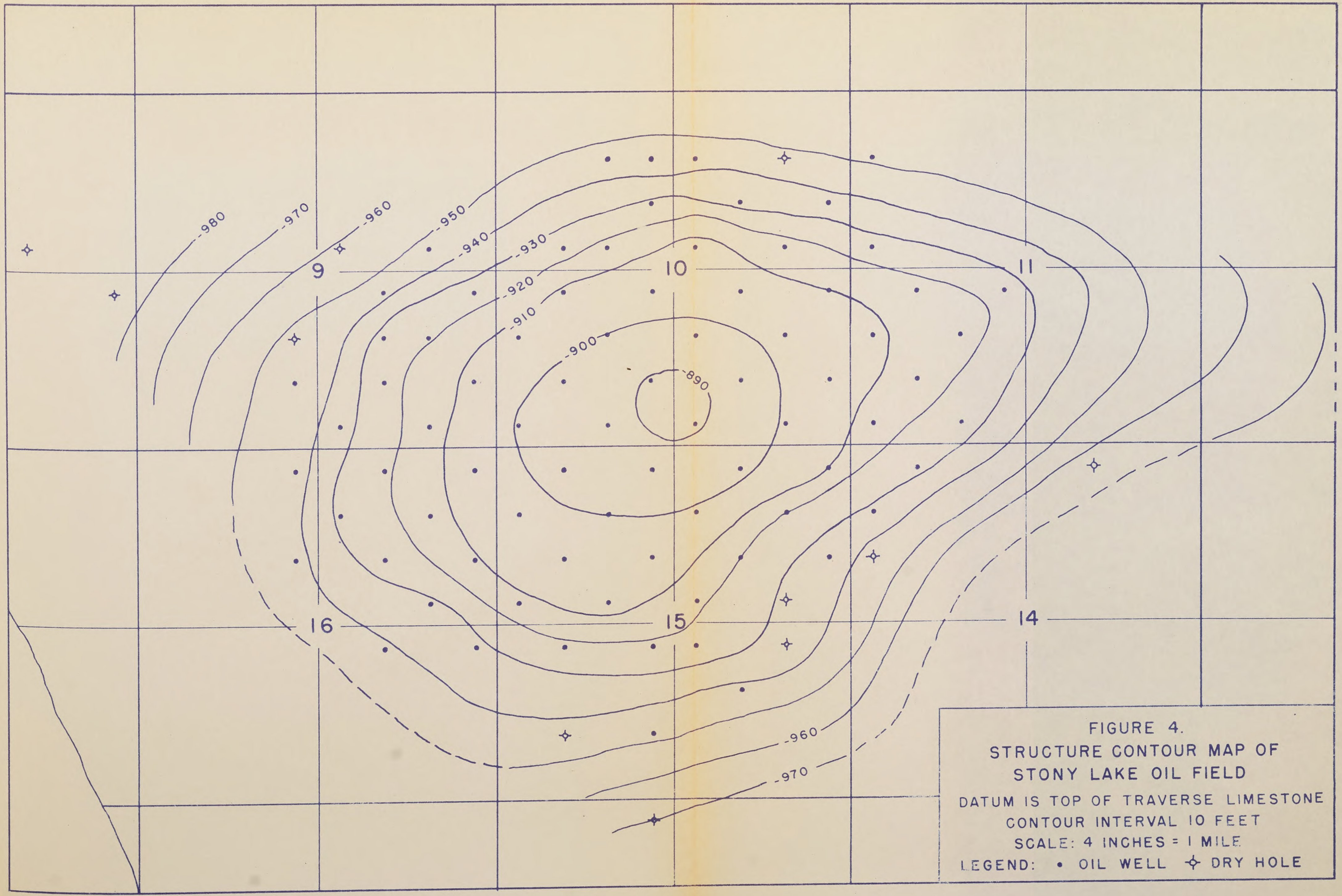

FIGURE 4.

STRUCTURE CONTOUR MAP OF STONY LAKE OIL FIELD

DATUM IS TOP OF TRAVERSE LIMESTONE

CONTOUR INTERVAL 10 FEET

SCALE: 4 INCHES = 1 MILE

LEGEND: • OIL WELL ⌖ DRY HOLE

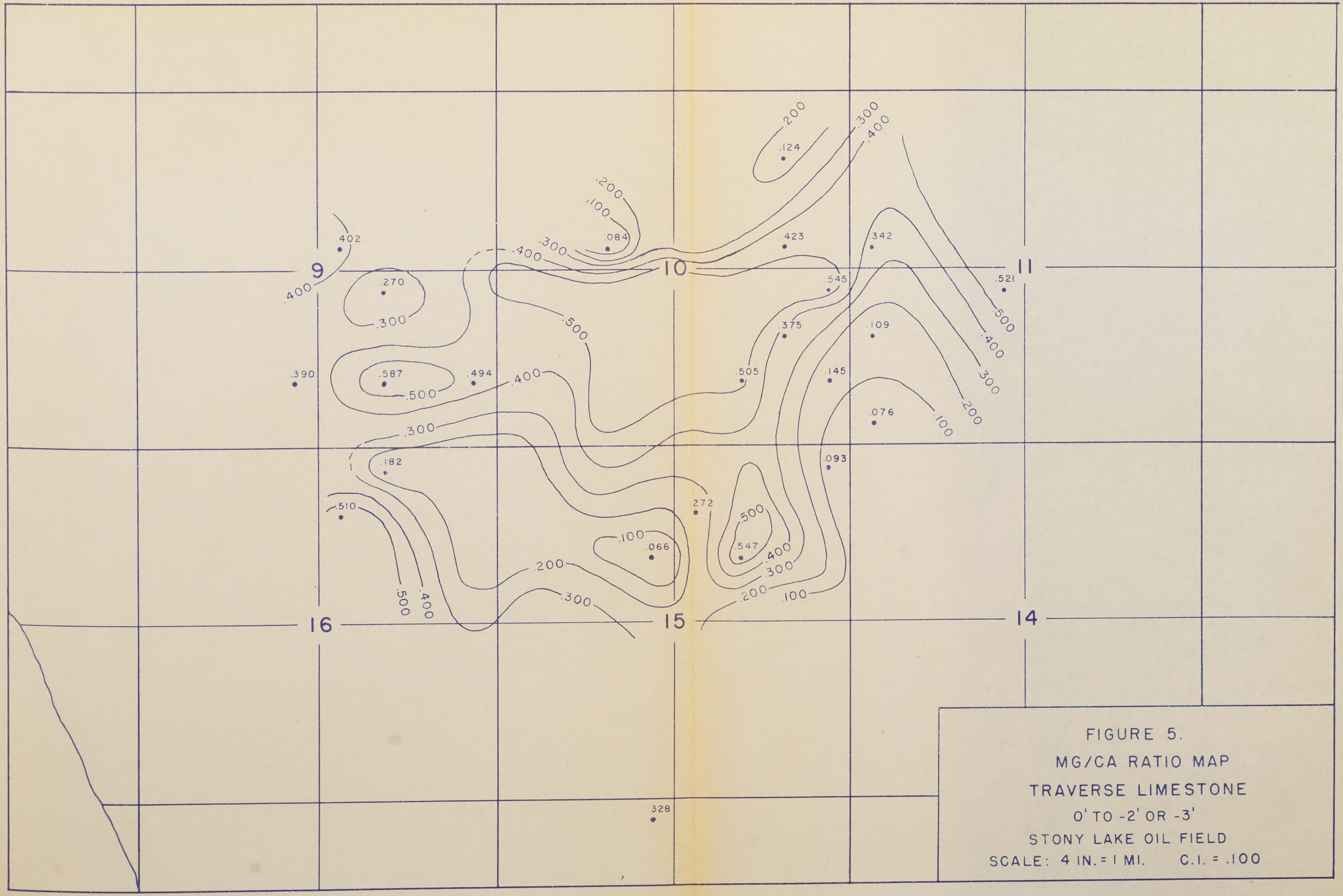

FIGURE 5.

MG/CA RATIO MAP

TRAVERSE LIMESTONE

0' TO -2' OR -3'

STONY LAKE OIL FIELD

SCALE: 4 IN. = 1 MI. C.I. = .100

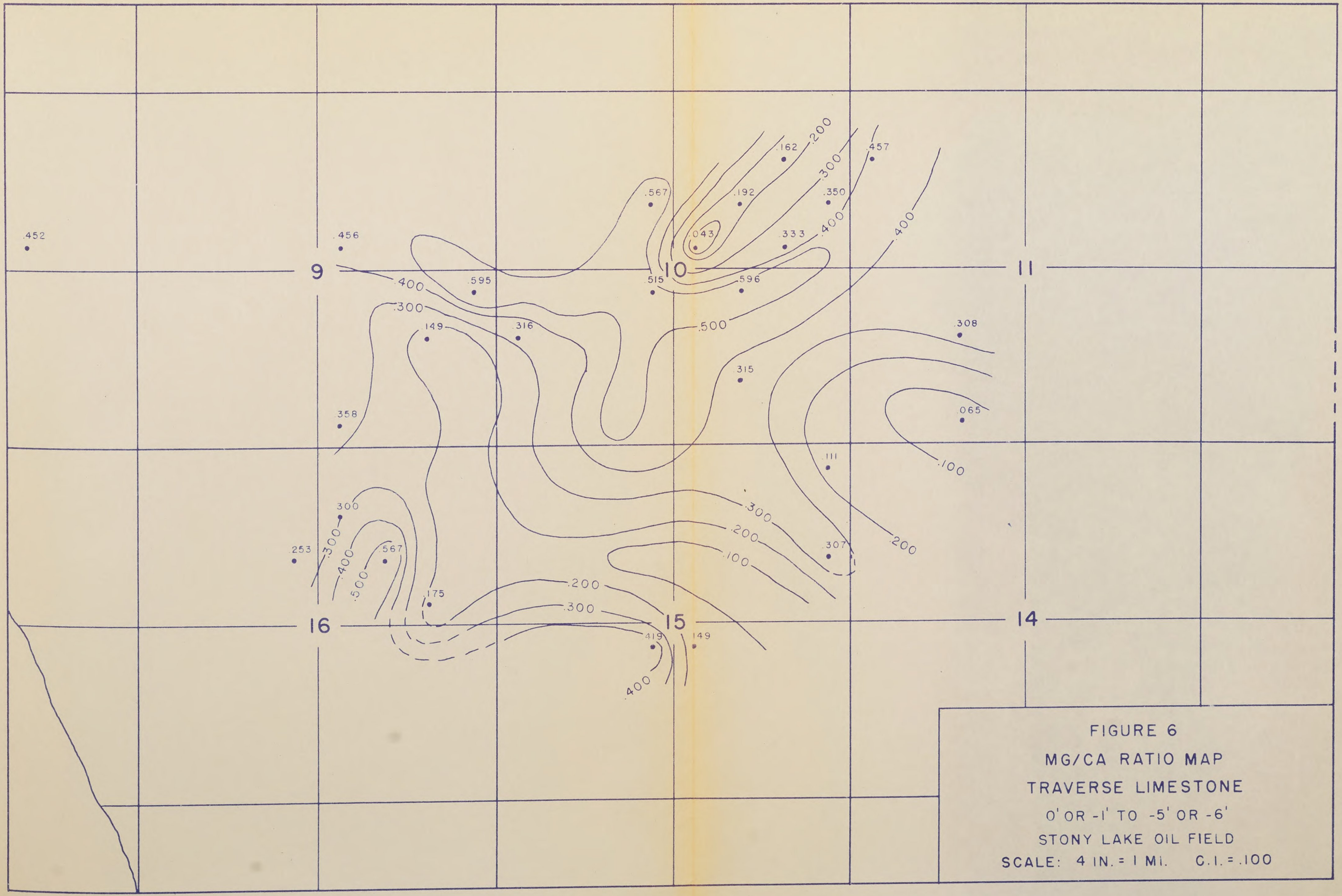

FIGURE 6

MG/CA RATIO MAP

TRAVERSE LIMESTONE

0' OR -1' TO -5' OR -6'

STONY LAKE OIL FIELD

SCALE: 4 IN. = 1 MI. C.I. = .100

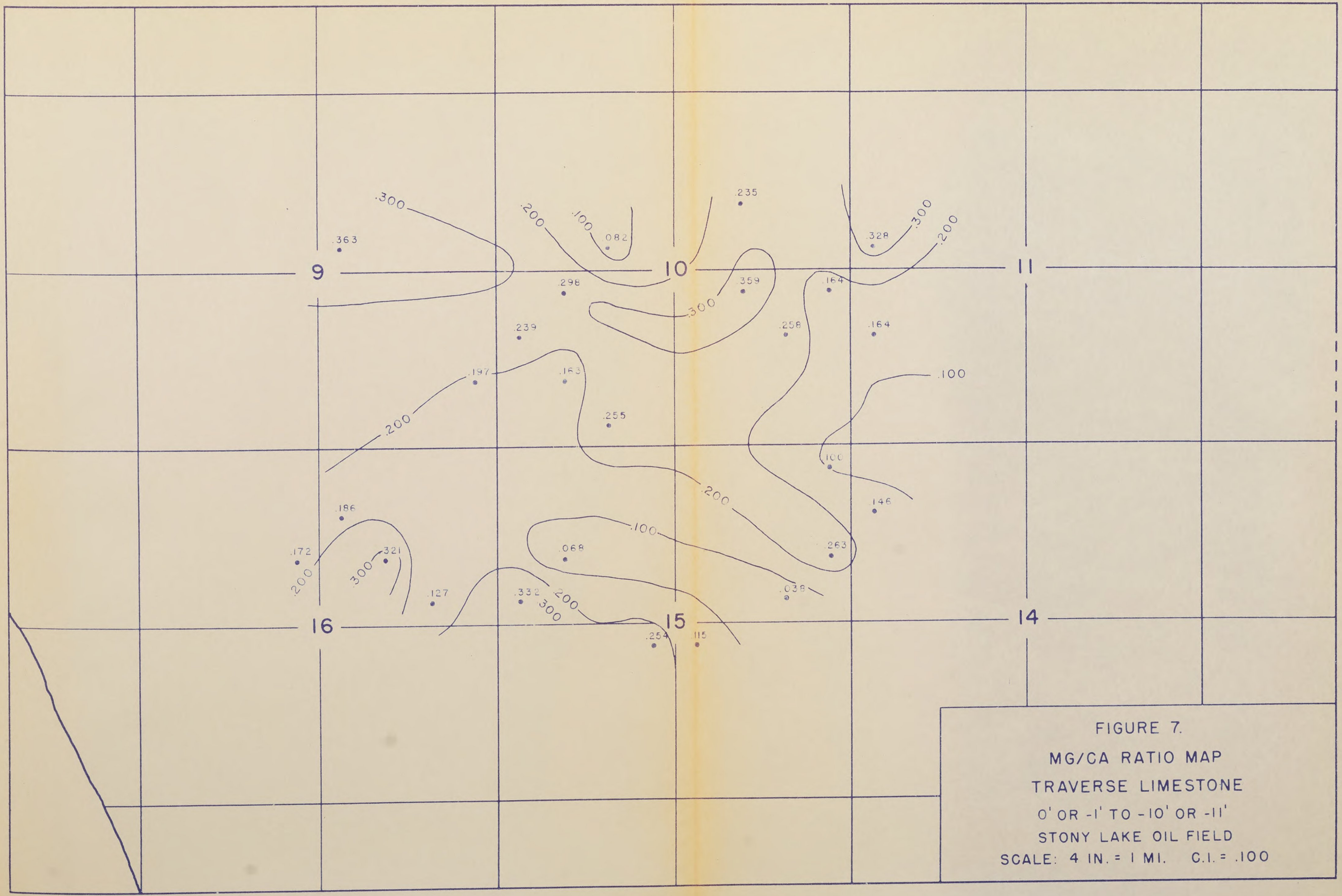

FIGURE 7.
MG/CA RATIO MAP
TRAVERSE LIMESTONE
0' OR -1' TO -10' OR -11'
STONY LAKE OIL FIELD
SCALE: 4 IN. = 1 MI. C.I. = .100

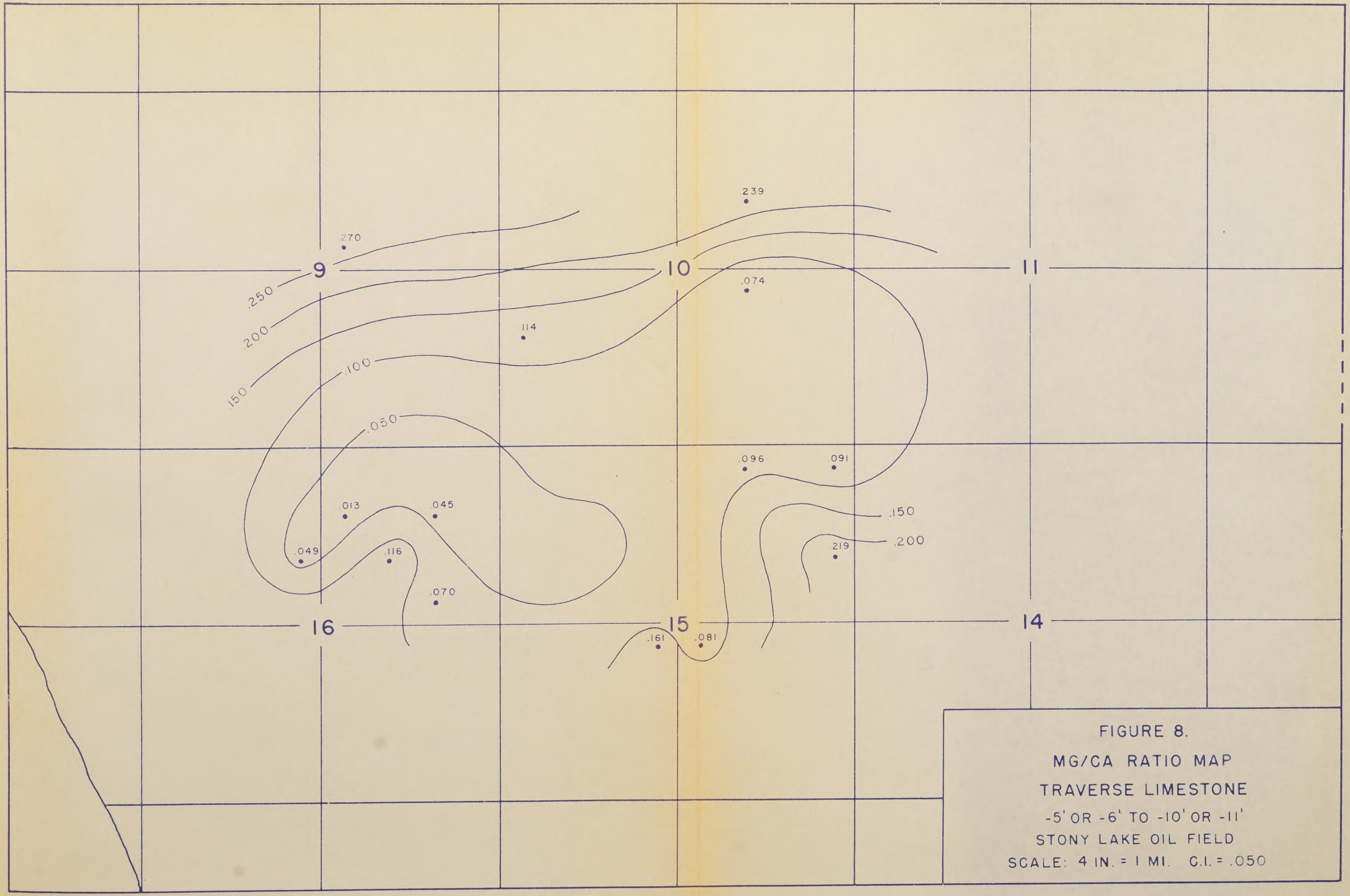

FIGURE 8.
MG/CA RATIO MAP
TRAVERSE LIMESTONE
-5' OR -6' TO -10' OR -11'
STONY LAKE OIL FIELD
SCALE: 4 IN. = 1 MI. C.I. = .050