A CHEMICAL, STATISTICAL AND STRUCTURAL ANALYSIS OF SECONDARY DOLOMITIZATION IN THE ROGERS CITY - DUNDEE FORMATION OF THE CENTRAL MICHIGAN BASIN

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Betty M. Tinklepaugh
1957

This is to certify that the

thesis entitled

"A Chemical, Statistical and Structural Analysis
of Secondary Dolomitization in the Rogers-City
Dundee Formation of the Central Michigan Basin."

presented by

Betty M. Tinklepaugh

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Geology

B. T. Sandefur
Major professor

Date ~~December 2, 1957~~

O-169

A CHEMICAL, STATISTICAL AND STRUCTURAL ANALYSIS OF SECONDARY DOLOMITIZATION IN THE ROGERS CITY-DUNDEE FORMATION OF THE CENTRAL MICHIGAN BASIN

by

BETTY M. TINKLEPAUGH

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Geology

Year 1957

Approved: B. T. Sandefur

BETTY M. TINKLEPAUGH

ABSTRACT

The Rogers City-Dundee (Devonian) formation in the central Michigan basin, although normally a marine limestone, is in many places an extremely porous dolomite. Oil fields producing from the Rogers City formation are generally limited to these dolomitic zones. The origin and characteristcs of these dolomitic zones were the primary concern of this investigation.

A study of the possible relationships between secondary dolomitization, structure, and porosity was made over an area of approximately 400 square miles chosen in the Central Michigan basin where four major fields produce oil from the Rogers City formation.

Chemical analyses for calcium, magnesium, and iron content were made from samples within the top twenty feet of the Rogers City formation, in which the pay zones occur. The methods used were adopted by the author from Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, published by the American Public Health Association, 1955. They were as follows:

1. Calcium analyses were made by the "Compleximetric" or versene titration methods as used for the determination of calcium hardness of water.
2. Magnesium and iron analyses were determined by spectrophotometric methods as adopted from water hardness tests.

These methods were highly accurate and extremely rapid as adapted for mass technique analyses.

Structural interpretations were made by an interpolation of a structure contour map of the area. Comparisons of this map with lithologic magnesium to calcium ratio maps were made to determine vertical and lateral relationships between structure and degree of dolomitization.

Statistical comparisons of the data were made by means of analysis of variance methods to determine relationships between: (1) dolomitization and structure, (2) dolomitization and porosity, (3) dolomitization and iron content of the limestones.

It was concluded from chemical analyses, structural and lithologic Mg/Ca ratio maps, and statistical analyses that in the top twenty feet of the Rogers City formation, including the prolific Coldwater oil field, there is a definite relationship between the degree of dolomitization and the magnitude of structure; there is a relationship between dolomitization and porosity, the nature of which is neither simple nor direct; and, there would appear to be an inverse relationship between iron content and the degree of dolomitization.

The magnesium-calcium ratio in limestones is a very useful geologic tool. It is especially useful in porosity studies and the location of dolomitized zones and structures.

The rapid and accurate techniques used in this study can enable geologists and petroleum engineers to make the Mg/Ca ratio determinations a routine analysis. Statistical studies may enable them to predict porosity of carbonate rocks and show the relationship between porosity and dolomitization for many limestones as yet unstudied.

A CHEMICAL, STATISTICAL AND STRUCTURAL ANALYSIS OF SECONDARY DOLOMITIZATION IN THE ROGERS CITY-DUNDEE FORMATION OF THE CENTRAL MICHIGAN BASIN

by

BETTY M. TINKLEPAUGH

A THESIS

Submitted to the School of Graduate Studies of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Geology

Year 1957

ACKNOWLEDGMENTS

The author wishes to express her sincere thanks to Dr. B. T. Sandefur for his aid and helpful suggestions throughout this investigation. The writer is greatly indebted to Mr. Irving L. Dahljelm of the Microbiology department for his advice in the development of the methods used for the chemical analyses and for the use of his laboratory facilities, equipment, and reagents.

Grateful acknowledgment is also due to Dr. W. D. Baten of the Statistics department for his suggestions and assistance in the choice of statistical methods employed and statistical interpretations best fitted to this study; and to Dr. Justin Zinn for a critical reading of the manuscript.

The writer wishes to thank G. D. Ells of the Michigan Geological Survey who generously assisted in obtaining well samples and necessary information required for this study. The author is grateful to Dr. A. M. McCarthy for assistance in editing the manuscript.

VITA

Betty M. Tinklepaugh

candidate for the degree of

Doctor of Philosophy

1957

Dissertation: A Chemical, Statistical and Structural Analysis of Secondary Dolomitization in the Rogers City-Dundee Formation of the Central Michigan Basin

Outline of Studies:

Major subject: Geology
Minor subject: Statistics

Biography:

Born: April 23, 1930, Corunna, Michigan

Undergraduate Studies: Central Michigan College, A. B. degree, 1948-1952

Graduate Studies: Michigan State University, Master of Science degree, 1952-1955; cont. 1955-57.

Experience: Graduate Assistant, Michigan State University, Geology department, 1954-1955, Natural Science department, 1956-1957; Graduate Council Fellowship 1953-1954 and 1955-1956; Cartographer, McClure Oil Co., summers 1954, '55; Instructor in Extension teaching in Geography, Michigan State University, summer 1955; Instructor in Natural Science, Michigan State University,1957

Affiliations: Member of the Geological Society of America, Michigan Academy of Science, American Association for the Advancement of Science, Michigan Geological Society, Sigma Delta Epsilon, Associate member of Society of Sigma Xi

TABLE OF CONTENTS

Page

LIST OF TABLES

Table Page

LIST OF FIGURES

LIST OF MAPS

INTRODUCTION

General

In Michigan a considerable number of petroleum fields produce from porous zones in locally dolomitized limestones. The Rogers City-Dundee (Middle Devonian) formation, in the central Michigan basin, is normally a fossiliferous, marine linestone, with no effective porosity. Penetration of the formation reveals that the upper 10 to 20 feet has been altered locally in many places to a porous dolomite from which a large quantity of oil has been obtained.

It is the belief of many geologists that the occurrence of secondary dolomitization is related to zones of weakness, tensional cracks, faults, fissures and the apices of folded structures within the limestone formations (Geikie, 1893; Steidtmann, 1917; Hewett, 1931; Hatch, 1938; Landes, 1946; Jodry, 1955). Because of the great amount of "commercial" porosity which is restricted to dolomitic facies within limestones, there has been a growing tendency for geologists to relate porosity to the process of dolomitization. Lauer (1917) attributed some porosity in petroleum reservoir rocks as due to "dolomitization cavities in altered limestones." Landes (1946) believes that the process of dolomitization and porosity is genetically related and refers to it as "local dolomitization porosity." R. B. Hohlt (1948) pointed out that "there is no agreement concerning the origin of porosity through diagenetic and epigenetic dolomitization" but "that a relationship exists between porosity and the process or processes of dolomitization, although no specific relationships have been established." In recent studies Chilingar and Terry (1954) conclude that "field evidence suggests that some porosity forms through dolomitization." On the other hand, J. E. Adamd (1934) stated: "The constant use of dolomitization as an explanation of the increase in porosity in limestone is one of the theories that appear to be overworked."

Problem

In an attempt to study the possible relationships between secondary dolomitization, structure, and porosity the author chose an area of approximately 400 square miles in the central Michigan basin in which fields producing oil from the Rogers City formation are generally limited to dolomite zones.

A chemical analysis of the Rogers City limestones from the well samples was made to determine the calcium, magnesium and iron content. The calcium and magnesium were recorded for the purpose of determining the Mg/Ca ratio as a measure of the degree of dolomitization of the limestone.

D. F. Hewett (1928) recorded that "dolomitized limestones contain more iron than the original rock." Steidtmann (1917), Tarr (1919) and Cheng, Kuang, and Bray (1952) confirmed this in individual observations of dolomitized limestones. But Hewett (1931) found "no evidence of increase in iron oxide with the process of dolomitization in the Goodsprings quadrangle of Nevada." Because of the possibility of a relationship existing between iron and dolomitization, the author included a determination of the iron content of the limestones in the chemical analysis.

A structural interpretation of the area studied is compared with lithologic Mg/Ca ratio maps to determine the possible relationship between structure and degree of dolomitization both vertically and laterally. Statistical comparisons are made to determine relationships between: (1) dolomitization and structure, (2) dolomitization and porosity, and (3) dolomitization and iron content of the limestones.

In order to determine more exactly the degree of dolomitization and iron content in the dolomitized limestone formation the author applied methods for the determination of calcium, magnesium, and iron from the approved procedures in <u>Standard Methods for the Examination of Water, Sewage, and Industrial Wastes</u> published by the American Public Health Association, 1955. These methods were accurate and easily adapted to mass analysis techniques.

HISTORICAL RÉSUMÉ OF DOLOMITE

Deodat Dolomieu, born in Dolomieu, France, was the first to describe the magnesium carbonate mineral which he discovered while making an extended tour among the Alps in 1791 (Knight, 1921). In the following year Saussure gave it the specific name of "dolomite" in honor of its first describer (Van Tuyl, 1914).

From this date unto the present the nature and origin of dolomite has been the subject of much discussion, the topic of many debates, and the object of many theories. In fact, it was noted by Van Tuyl (1914) that Arduino, in the year 1779, made the first attempt to explain the formation of "magnesium limestones" by pneumatolytic alteration of pre-existing calcite limestones in an area of volcanic activity.

Voluminous literature has appeared on the subject of dolomite origins and many theories have been proposed since its discovery. For more than a century recognition of the presence of exceptional porosity in many dolomites has been associated with theories on the origin of this rock. The importance of porosity to the petroleum industry is a known and established fact. The possible relationship then of the origin of dolomites and dolomitization to that of porosity has become an increasingly important problem to

the petroleum geologist and an added stimulus to a continuing interest in the nature of dolomites.

Although much has been written in regard to the many origins of dolomite and their relationship to porosity, only a brief résumé of the history and present status of the problem, as related to the one at hand, will be given here.

The theories of the origin of dolomite may be classified conveniently in the following manner:

I. Primary deposition theories
    A. Chemical
    B. Organic
    C. Clastic

II. Alteration theories
    A. Marine alteration
    B. Ground water alteration
    C. Pneumatolytic alteration

III. Leaching theories
    A. Marine leaching
    B. Surface leaching

I. Primary Deposition

A. Chemical Theory

This theory, that dolomite is an original chemical precipitate on the sea floor, has had many followers, and some geologists still adhere to it today. Boné advocated this method of origin as early as 1831, and Bertrand-Geslin (1834) was an early supporter of this theory. Similarly Wagner (1839) favored the theory that the dolomites of the French Jura were original deposits rather than

alteration products. Coquand (1841), however, concluded that dolomite had a two-fold origin, being in part a regular chemical precipitate on the sea bottom, and in part the product of the action of volcanic agents on limestone. Wissmann, about this time, expressed the belief that the dolomites of the Tyrol were original deposits, and Petzholdt stated that "both the dolomite and the limestone of this region are chemical precipitates, since they grade into each other" (Bischof, 1859). This, Petzholdt believed, would account for the predominance of limestone in the lower part of the section and of dolomite in the upper, since $MgCO_3$ is the more soluble of the two carbonates and would be the last to be "thrown out" of solution. Fournet (1849) likewise interpreted the dolomite of the same region as an original chemical precipitate.

Forchhammer (1850), soon after, pointed out that certain dolomitic nodules in the Cretaceous limestones at Faxö were probably chemical. These he believed to be the product of the reaction of the $CaCO_3$ of spring water with the magnesia of sea water. The presence of material resembling travertine in the rocks and other evidences of spring action seemed to lend support to this theory.

Delanoue (1854) was inclined to favor the chemical precipitation theory for dolomites in general, regarding secondary dolomites as only local and of little importance.

Hunt (1859) also expressed himself unequivocally in favor of the chemical precipitation of dolomite, giving as his opinion, that "dolomites, magnesites, and magnesian marls have had their origin in sediments of magnesium carbonate formed by the evaporation of solutions of bicarbonate of magnesia."

Cordier (1862), approaching the problem from a philosophical standpoint, was also led to believe dolomites were chemical deposits, and Leymerie (1864) entertained similar beliefs. He pointed out that the dominant salt in the sea today is NaCl, while $MgCl_2$ and $CaCl_2$ are accessory, but supposed that in early Paleozoic time conditions may have been reversed.

Von Rosen claimed chemical precipitation as the probable method of origin of the dolomite and dolomitic limestone of the Düna and Welikaja regions in Finland and Kurland, and Gümbel applied it to the dolomites of the French Jura and of the southern Tyrol. Zirkel (1894) and Scheerer (1866) believed that all of the oldest dolomites represent chemical precipitates.

Loretz (1878) also favored the view that the dolomites of the southern Tryol were original formations and leaned towards the chemical theory. The preservation of fine and detailed structures in the rock suggested to him its primary nature.

S. F. Emmons (1886) adopted the primary theory for the origin of dolomites of the Leadville district, Colorado.

He concluded that "the magnesia is an original constituent of these rocks, having been deposited at the same time as the lime." Later, Vogt (1898) came out in favor of this view, stating that certain Norwegian dolomites were chemical. Ulrich and Schuchert (1901) have also implied that certain dolomitic limestones were chemical.

The chemical theory has had one of its greatest champions in Suess (1906), who points out "that in the Plattenkalk formation beds of dolomite, often containing more than 40 per cent $MgCO_3$ and of constant thickness and regular contacts, are interbedded with limestone," and maintained that "the dolomite was deposited as such from the sea."

The chemical theory, however, has been elaborated most fully by Daly in two very descriptive papers. In the earlier paper (1907) this writer pointed out that in Pre-Cambrian time, when the scavenger system of the ocean was not yet developed, the seas must have been depleted in lime and magnesia due to the precipitating effect of $(NH_4)_2CO_3$ generated from decaying organisms on the sea bottom. "The magnesium carbonate should have been most abundantly thrown down in Pre-Cambrian time; its precipitation must have been lessened through Paleozoic and Mesozoic time and has reached its minimum since the abysses of the ocean became abundantly tenanted with scavengers" (Daly, 1907). In Daly's second paper (1909) this theory was developed still further. The

alternation of clean-cut beds of limestone with beds of magnesian limestone or dolomite, as illustrated by the Pre-Cambrian formations of British Columbia and Montana, also seemed to him to speak for the original deposition of the two carbonates as against later metamorphism or alteration.

Following closely upon Daly came Linck (1909) as an advocate of the chemical precipitation theory. Basing his conclusions upon the conditions of his experimental production of dolomite, he also assumed "that $(NH_4)_2CO_3$ derived from the decay of marine organisms was a competent precipitating agent."

Two years later Steidtmann (1911) concluded a comprehensive study of dolomites with the following statement: "Dolomite develops predominantly in the sea, therefore the decrease in the dolomite content of the sediments in going up the geologic column is mainly due to a decrease in the proportion of dolomite developed in the sea with time."

Another investigator to express himself as favoring the chemical hypothesis was Weigelin (1913), who applied it to the dolomites associated with salt and gypsum in the Lower Keuper of West Württemberg. The upward succession of dolomite, gypsum, and salt here suggested to him that all these were the products of evaporating seas.

W. A. Tarr (1919, 1920) also considered dolomite to be a chemical precipitate from shallow marine waters. He believed freshing of the waters to be the cause of interbedded pure limestones alternating with the dolomites in shallow, inclosed seas. Similarly, Stauffer and Thiel (1933) believed that the direct chemical precipitation from sea water may have been the process in a few cases of dolomites in Minnesota but that it is no longer a major one in the present sea.

Late investigations by W. Stout (1941) of the dolomites of western Ohio have lead him to the conclusion that "the dolomites are marine in origin, were deposited in shallow or comparatively shallow water, and in the main are direct precipitations . . . most certainly they were laid down in the form we now find them and are not secondary . . . ."

Recent studies have been made by geologists concerning present day conditions under which dolomites may be forming by direct chemical precipitation. A. J. Eardley (1938) and P. Weaver (1946) have published results favorable to this theory under conditions of high concentrations and excessive evaporation of the waters studied.

B. Organic Theory

The opinion formerly prevailed in some quarters that organisms have played an important role in the formation of dolomite.

Forchhammer showed by a series of analyses as early as 1850 that the calcareous skeletons of some organisms contained considerable magnesia. The chemical studies of

Damour (1851) also led him to support this theory. Analysis of calcareous algae ("corals") by him showed a high $MgCO_3$ content in four out of six specimens. Damour concluded, therefore, "from the development such forms take on along the shore and on the sea bottom that deposits of magnesian limestone are being formed by them today and must have been formed by them in the past."

Ludwig and Theobold (1852) also emphasized the importance of algae in the deposition of limestone and dolomite. In the travertine of the mineral spring at Nauheim, in the Wetterau, which is deposited through the agency of algae, these writers found a magnesia content ranging up to 11.69 per cent.

The observations of Doelter and Hoernes (1875), who held that many "weakly dolomitic limestones" were deposited directly in the sea through the activity of organisms, were also in accord with the organic theory.

Late investigations by Wallace (1913) tended to lend weight to this theory, since he believed "that the occurrence of dolomitic fucoid-like markings in the Ordovician limestones of Manitoba is best accounted for on the assumption that algae, bearing considerable magnesia, were imbedded in the rock at the time it was deposited and that this magnesia was influential in producing local dolomitization of the limestone." Nadson and Walther (1916) advanced the suggestion that the presence of bacteria in the sea water may possibly influence the process of dolomitization.

C. Clastic Theory

That some dolomites may represent ordinary mechanical sediments derived from the erosion of older dolomitic limestones, seems to have been conceived first by Lesley, in 1879. He suggested this mode of origin for an interbedded series of limestones and dolomites of the "Calciferous," exposed in the old Walton quarry, on the west bank of the Susquehanna river, opposite Harrisburg, Pennsylvania.

Such a theory of origin was favored by Phillip (1907) to account for certain impure dolomites associated with clastic sediments in the Muschelkalk of Germany. He believed "that the material constituting these dolomites probably was derived from the residuum of a limestone originally low in magnesia." This view has been adopted by Grabau (1913) who holds that "the upper Silurian waterlimes and certain dolomitic intercalations in the Salina are clastic deposits derived from the erosion of older limestones." The same writer (1913) was of the opinion "that certain interstratifications of limestone and dolomite likewise are explainable upon the basis of the clastic theory," remarking that "the relationship is most satisfactorily explained as a primary difference in the materials deposited, that both the limestone and the dolomite are clastic but are derived from different sources, or that the limestone is organic and the dolomite clastic" (Grabau, 1913).

II. Alteration Theories

A. Marine Alteration

The theory that dolomite has had its origin in the alteration of limestone before it emerged from the sea has had many followers and probably is most widely held today. Among the supporters of this view there has been almost unanimous agreement that the sea water contributed the magnesia. An exception to this is the view of Favre (1879) who, basing his suppositions upon the conditions of the experimental production of dolomite by Marignac, concluded that "the dolomites of the Tyrol were formed by magnesium compounds furnished by the action of sulphurous and hydrochloric acids of volcanic origin on the lava of submarine melaphyr eruptions."

The concept that the alteration might be effected by the magnesia of sea water was first suggested by Dana (1843), to account for the dolomitic reef rock of the coral islands of the Pacific. He hinted, at the time, that "the rock might have been formed by the introduction of magnesia through the medium of heated sea water which possibly contained a larger supply of this element than usual." In 1872, Dana expressed the view that "the same dolomite had been formed in sea water at ordinary temperatures but perhaps in a concentrated state." In the 4th edition of Dana's Manual, (1895) this same idea is elaborated without modification, the opinion being held that the concentrated brines in the lagoon would contain $MgCl_2$ and $MgSO_4$ in a state favorable to the formation of dolomite.

F. Pfaff (1851) likewise regarded the marine alteration theory as the most practicable for the origin of the dolomites of the French Jura.

Sorby (1856) expressed himself in favor of the marine alteration theory when he suggested that the formation of certain dolomites was effected by the alteration of limestone through the agency of soluble magnesian salts of the sea water "under some peculiar conditions not yet clearly explained during the period when it became so far concentrated that rock salt was frequently deposited . . . ."

Similarly, Von Richthofen adopted this theory, in 1860, to explain the formation of the great dolomitic reef rocks of southern Tyrol (Skeats, 1905). He claimed that "these dolomite masses represent dolomitized coral reefs formed during a period of subsidence and that the St. Cassian marly and tuffaceous deposits which flank the reefs represent the deposits of lagoons, bays and channels of the coral sea." R. Harkness (1859) commented along these same lines on the dolomites formed along the jointings in the Devonian rocks around Cork as being due to "magnesium salts in sea water . . . over consolidated and already jointed limestones . . . causing dolomitized rock along joints, fractures, and bedding planes in limestones."

Mojsisovics (1879), in his classic memoir on the dolomite reefs of the same region of Tyrol, proposed a theory not essentially different from that of Von Richthofen. He held that the dolomite masses represented altered coral reefs possibly formed in the same manner as the one described by Dana, but doubted if the sea which effected the alteration was concentrated in lagoons as postulated by that writer.

Hoppe-Seyler (1875) was also a champion of the marine alteration theory. He believed that the magnesia for altering great limestone masses to dolomite could be furnished only by the sea. In like manner, Doelter and Hoernes (1875) supported this theory in their memoir on dolomite building, attributing the greater part of the dolomites, more or less rich in magnesia, to the action of magnesia of sea water, especially the $MgCl_2$, on limestone made up of the calcareous skeletons of organisms.

F. W. Pfaff (1894), basing his evidence upon the conditions under which he prepared dolomite artifically, concluded that coral reefs might be altered to dolomite. The paucity of fossils in some dolomites was attributed by Pfaff to the fact that the sea may have been in a concentrated state when they were deposited. He, therefore, believed that dolomitization took place contemporaneously with deposition in some cases and in support of this he cited analyses showing a high magnesia content in slimes dredged from a considerable depth in the modern seas.

The view that pressure induced by considerable depth is an important factor in dolomite formation, however, was not shared by Phillipi (1907), who pointed out that "dolomite is associated with sandy sediments in the Röt and Keuper and that the presence of calcareous algae in the dolomite of the Alpine Trias proves that this could not have been formed in a deep sea as urged by Pfaff, since algae seldom live below 80 fathoms and never so deep as 200 fathoms." Moreover, Phillipi cited evidence of dolomitization at shallow depths and at ordinary concentration in the modern seas.

The dolomites of the Aspen District of Colorado were best explained upon the basis of the marine alteration theory, according to Spurr (1898), who expressed himself as follows: "The Silurian dolomite . . . was originally deposited in quiet seas, and was built up from calcareous sediments . . . these beds were subsequently altered to dolomite by the magnesium salts of a great evaporating shallow inland sea . . . ."

Calvin and Bain (1899) adopted an analogous explanation for the origin of the Galena dolomite of the upper Mississippi Valley. They stated that "it looks as if dolomitization had affected the limestone . . . after the formation was complete; and that the depth to which the change descended was, in some instances and to some extent at least, determined by the presence or absence of impervious beds of shale."

Van Hise (1904), on the other hand, tended to minimize the importance of dolomitization before the limestones emerged from the sea and emphasized the importance of ground water as a dolomitizing agent.

Branner (1904) furnished evidence of recent dolomitization through the agency of sea water in an old reef rock of the stone reefs of Brazil. This rock was found to bear 12.98 per cent $MgCO_3$ and the assumption was made that part of the lime of the coral rock had been replaced by magnesium from sea water. The rock is still within reach of sea water, and dolomitization was believed by him to be still in progress.

Several examples of altered coral reefs have been described by Skeats (1903) from the southern Pacific. Dolomite occurs in several of the elevated coral islands there, but attains its greatest purity on Christmas Island, where it contains as much as 43.3 per cent $MgCO_3$. This author held that "Dana's theory with some modification probably applied here," and he believed that "the view that limestone is altered dolomite at a considerable depth corresponding to a particular pressure is untenable." Skeats (1905) was one of the first to recognize both "local" and "regional" dolomitization and different causes for each.

Other examples of dolomitization believed to have been effected by sea water have been described by Dixon (1907) as occurring in the Carboniferous limestones of South Wales.

Peach and Horne (1907) were of the opinion that the Cambrian dolomites of the Northwest Highlands of Scotland were formed by the dolomitization of calcareous sediments on the sea bed itself; but they regarded it as possible that "there may have been also an enrichment of magnesia through the leaching out of the more soluble calcareous material of a slightly magnesian ooze, possibly made up of the secretions of unicellular plants of the plankton."

The marine alteration theory was adopted likewise by Salomon (1908) to explain certain nests and tongue-like extensions of dolomite in the Ladinic limestones of the Alps. Similarly Walther (1908) recognized that dolomites may be produced in this manner.

In favor of some method of alteration capable of operating over wide areas were the observations of Weller (1911), who, from a comparison of the faunas of the Galena and Niagaran dolomites of the Upper Mississippi Valley with their non-dolomitized equivalents in other regions, concluded that they must have been deposited first as limestone and later metamorphosed.

Blackwelder (1913) also advocated this method of origin for the Bighorn dolomite of Wyoming; but the low porosity of the dolomite (1.31 per cent) and its sharp contact with the limestone interbedded with it and underlying it lead him to favor the belief that "it was not formed by the substitution of magnesium for half the calcium in normal limestone, but that it has resulted from progressive alteration during deposition." In this particular, then, Blackwelder followed Daly (1909), who believed that the magnesia content of the pre-Devonian limestones was original and that "in many, if not all, cases the dolomite crystals may have been formed at or near the surface of the ancient calcareous muds by the interaction of the magnesium salts of sea-water with the more easily precipitated calcium carbonate."

The later beliefs of Nahnsen (1913) likewise were in line with the theory of the alteration of limestone beneath the sea. He described a horizontal seam of dolomite with wavy boundaries in the Upper Jurassic limestone of North Germany, and concluded that "the alteration probably took place beneath the sea before the rock solidified, since solutions would not circulate freely after recrystallization."

F. M. Van Tuyl (1914, 1915, 1916) held that "the great majority of the dolomites, from Cambrian to present, have resulted from the replacement of limestones before they emerged from the sea." "The replacement need not be accompanied by shrinkage, but may proceed according to the law of equal volumes, as enunciated by Lindgren (1912)." "Certain cases of apparent inter-stratification of limestone and dolomites cited as evidence in favor of some primary theory are rather pseudo-inter-stratifications, which have resulted from selective dolomitization." "Examples of limestone mottled with dolomite were interpreted as representing an incipient stage in the process of alteration." "Organic factors have exerted a selective influence in some cases of mottling, but in others the phenomenon is purely inorganic" (Van Tuyl, 1914).

E. Steidtmann (1917) stated that "the majority of dolomites developed in the sea as a sediment either by direct precipitation or by reactions within the limy sediments of the sea bottom."

E. W. Skeats (1918) believed that he himself was the first to develop the hypothesis of a very shallow water origin for "contemporaneous" or "regional dolomites."

Other examples of dolomitization believed to have been effected by marine alteration have been described by Clark (1924) and by Stauffer and Thiel (1933). The latter stated that "the process of dolomitization must be considered one of enrichment rather than of original deposition." "Dolomitization thus appears to have been due largely to a replacement of part of the calcium in the original more or less pure calcium carbonate, probably before the resulting rock had been completely consolidated."

H. R. Greiner (1956) believed the "evidence for replacement overwhelming." He suggested that "contemporaneous or penecontemporaneous dolomitization took place on the sea floor under reducing conditions in shallow, warm marine waters of high salinity." This theory has likewise been adopted by Pettijohn (1949).

B. Ground Water Alteration

That ground water is capable of accomplishing local dolomitization under favorable conditions there can be no doubt, and there has been a tendency on the part of some to believe that this method of alteration is of far-reaching significance. Most writers who have supported this view have emphasized the importance of the $MgCO_3$ of ground water as the dolomitizing agent, but some have advocated that $MgSO_4$ was very effective. For instance, Collegno, as early as 1834, pointed out the frequent association of gypsum and dolomite in the St. Gothard region and regarded these both as transformation products resulting from the action of the $MgSO_4$ in surface water on limestone. For similar reasons Haidinger (1827) advocated this method of origin, but since he found evidence that "under ordinary conditions a solution of $CaSO_4$ tends to convert dolomite into $MgSO_4$ and $CaCO_3$" he assumed that the contrary change takes place at great depths and under considerable pressure.

Haidinger (1827) first pointed out that dolomite might be formed by the partial replacement of calcite by magnesium carbonate and described a dolomite pseudomorph after calcite, intimating that it had been formed in this manner. It remained for Beaumont (1836), however, to put this theory into definite form. Reasoning on the basis that "the replacement was molecular and that one out of every two equivalents of $CaCO_3$ was replaced by $MgCO_3$" he calculated that "the transformation of limestone to dolomite should be accompanied by a decrease in volume of the rock to the extent of 12.1 per cent." This he believed would explain the cavernous character of the dolomites of the Tyrol. Actual porosity determinations of a sample of dolomite from the Alps by Morlot (1847), who obtained the value of 12.9 per cent, later seemed to confirm this prediction.

Scowler (1838) also favored this view for the origin of the Carboniferous dolomites of Ireland, believing that the alteration might readily be accounted for by the infiltration of water charged with $MgCO_3$. He suggested that the magnesia was derived from an igneous or ancient Paleozoic rock, or from springs.

Discussing the dolomite of the coral island of Metia, Jackson (1843) suggested that ascending spring water bearing $MgCO_3$ might have effected the change. Likewise, Haussmann (1854) believed that the dolomite of the Muschelkalk was produced by the action of $MgCO_3$ of ascending thermal springs on limestone.

It will be observed that most of the foregoing advocates of the ground water alteration theory attributed the source of the magnesia to spring water. An entirely different idea, however, was entertained by Green (1876), who suggested that the $MgCO_3$ might be furnished by the decomposition of olivene sand incorporated in the limestone at the time it was formed. It was his belief that "many magnesian limestones and dolomites as well as serpentinous streaks in limestone may have been formed in this manner."

There always has been a tendency to regard dolomite veins in limestone as the product of the reaction of the $MgCO_3$ of circulating ground waters on limestone. For instance, Schmidt (1875) expressed the view that the dolomitized limestone associated with the ores of the Joplin district was formed in this way. In like manner, Michael (1904) attributed the "dolomitization of the Muschelkalk along lines of disturbance at Tarnowitz, in southeastern Prussia," to the same cause. The dolomitization there appeared to be closely bound up with the mineralization phenomena, the sulphide ore deposits being limited to the dolomitic areas.

The local dolomitization effects in the Leadville limestone of the Aspen district of Colorado also were attributed to the action of the magnesia of ground water by Spurr (1898). The limestone is dolomitized along faults and fractures and "the local dolomitization almost invariably accompanies the ore."

Van Hise (1904) strongly emphasized the importance of dolomitization through the agency of ground water, and it would appear that he gave this method of dolomite formation precedence over dolomitization beneath the sea.

Local dolomitization phenomena along fissures in the Carboniferous limestone of South Wales was attributed to the action of ground water by Dixon (1907), who stated that water percolating downwards from the surface effected the change. Wichmann (1909) likewise had described local dolomitization effects in the Korallenoolith (Jura) which he ascribed to the action of ground water bearing $MgCO_3$.

E. Steidtmann (1911, 1917), expressing himself upon the efficiency of ground water in producing dolomitization, regarded "this method of dolomite building as capable of operating only locally."

R. A. Smith (1915) stated that "geologic evidence in favor of the replacement process is so strong that it has been commonly accepted as the dominant process in dolomitization."

D. F. Hewett (1928, 1931) has utilized the local dolomitization near lead and zinc deposits along fractures and minor partings as a local aid in searching for ore bodies.

F. W. Beales (1953) in his study of the dolomitic mottling in the Palliser (Devonian) limestone regarded it as the result of "secondary alteration and recrystallization in the rock." He believed that there was a "relationship between dolomitization and organiz remains in the limestone."

C. Pneumatolytic Alteration

The pneumatolytic theory of the origin of dolomite was introduced in 1779, by Arduino, to whom we are indebted for the first attempt to explain the formation of the rock.

Heim (1894) also entertained similar views as to the origin of the rock, but it remained for Von Buch (1847) to develop the theory and put it in definite form in the early twenties of the last century. In his studies in the Tyrol, he observed that "the dolomite was vesicular; that the bedding planes and the fossils were obliterated and that a brecciated, fissured and crystalline structure had been taken on." He, therefore, concluded that this could represent no original deposit from the sea, but that it must have been deposited at first as limestone and subsequently altered. This alteration, he believed, was accomplished by "volcanic vapors bearing magnesia, which were given off by the intrusions of augite porphyry which there penetrate the rock." This belief, however, was not shared by Wissmann (1859), nor by Fournet (1849), who were unable to find any constant association of the dolomite with the intrusives.

In 1843, Klipstein adopted the pneumatolytic theory to explain the veinlike deposits and irregular masses of dolomite in the transition limestone of the Lahn district, holding that "ascending magnesian vapors had effected the transformation," although he was not able to find fissures extending downwards from the dolomite in all cases (Bischof, 1859).

Karsten (1848) also favored the volcanic theory as elaborated by Von Buch. Frapolli (1841) similarly has gone on record in favor of this view, holding that "the dolomites

were formed through the agency of volcanic emanations either while deposition was going on beneath the sea or after the rock was deposited."

D. F. Hewett (1924) explained the dolomitization of rocks in the Spring Mt. Range of Southern Nevada as due to solutions from small intrusive bodies of orthoclase porphyry.

III. Leaching Theories

It has been long known that when a magnesian limestone is subjected to solvent action the lime is taken into solution much more rapidly than the magnesia, giving rise to a concentration of the latter constituent. Thus many geologists have held that by the continued leaching of a limestone originally low in magnesia, either at the surface or beneath the sea, a dolomite might in time result.

A. Surface Leaching

The belief that dolomite might result from surface leaching seems to have been first suggested by Apjohn (1838), who stated that "the $CaCO_3$ might be removed from limestones containing some magnesia by the solvent action of carbonated waters, and that some dolomites might have been produced in this manner." Grandjean subsequently was led to adopt the same explanation, in 1844, to account for the dolomites of the lower Lahn district, and he pointed out that the dolomite was developed to its greatest extent near fissures and cracks in the limestone where water had had easy access.

The same theory was accepted by Sandberger the following year for the dolomites of the same district.

In support of this theory are the observations of Bischof (1859), who showed by experiment that "carbonated waters do not dissolve out of magnesian limestone more than a mere trace of magnesia" and concluded "that dolomite would ultimately be formed either by the action of surface water, or of sea water on limestone."

Hardman (1875, 1877) also regarded this as the plausible theory of dolomite formation, and he sought by its employment to explain the method of origin of the Carboniferous dolomites of Ireland.

Later, Hall and Sardeson (1895) favored this theory in their discussion of the origin of The Magnesian Series of the Northwestern States. Phillipi (1907), in like manner, adopted the leaching theory to account for the Conchodon dolomite of the southern Alps.

E. Steidtmann (1911) recognized "a little dolomitization caused due to leaching or weathering of limestone and leaving magnesium behind."

C. B. Claypool and W. Howard (1928), in studying the relationship of calcite and dolomite in a sediment as a criterion for the recognition of an uncomformity, stated that "porosity is attended by a leaching of the calcite with a retention of the dolomite."

Recent studies by Thiel and Sherman (1938), however, attributed an enriched dolomitic zone in the glaciolacustrine silts of glacial Lake Agassiz to the work of ground waters rich in magnesium rather than a removal of the calcite with a retention of the dolomite.

B. Marine Leaching

That marine leaching of calcareous deposits low in magnesia might give rise to dolomite was suggested by Bischof in 1859, but he made no attempt to elaborate the idea. Eleven years later, Gümbel (1870), in making a study of certain deep sea oozes, found one taken from a depth of 2,350 fathoms in the Atlantic which yielded upon analysis 1.44 per cent magnesia. This magnesia content was accounted for upon the basis of the solution of a portion of the original calcareous material, and it was suggested "that by the same method dolomitic rocks and marly intercalations might be formed" (Van Tuyl, 1914).

The marine leaching theory, however, has been most fully developed by Högbom (1894). The writer regarded marine leaching as far more important than surfacing leaching, since the latter can operate only on that portion of the limestone exposed. Högbom also furnished evidence of enrichment of magnesia by marine leaching in the coral reefs of Bermuda.

Judd (1904) was of the opinion that the dolomitic rock disclosed by the boring at Funafuti was formed, in part at least, by marine leaching.

Peach and Horne (1907) were favorable to the idea that marine leaching may account in part for the Cambrian dolomites of the Northwest Highlands of Scotland, suggesting that "unicellular plants which secreted lime may have existed as plankton, as in the sea today, and that the small magnesia content of these may have been concentrated by the abstraction of the more soluble $CaCO_3$." They believed, however, that some replacement had also taken place.

Murray and Hjort (1912) concurred that the explanation of enrichments of magnesia in deep sea deposits was to be sought in preferential dissolution of the lime. Enrichment of the magnesia by reaction with sea water did not seem plausible to them, "since this would require that the waters be concentrated with $MgCO_3$."

New Classification

Inasmuch as there is no agreement among the American geologists as to the meaning of primary and secondary dolomites (Rodgers, 1954), it is necessary for anyone using these terms to specify what he means in order to be understood. For instance, another classification of dolomites has been adopted by Vishnyakov (1951), which includes three genetic types: (A) primary, (B) diagenetic, (C) epigenetic.

A. Primary Dolomites

Primary dolomites formed by direct chemical precipitation can be recognized easily when associated with other primary sediments. These dolomites lack primary porosity and caverns and are commonly interlayered with clays, marls, and gypsums (commonly containing pseudomorphs after gypsum), (Chilingar, 1956).

B. Diagenetic Dolomites

Diagenetic dolomites can be found in the form of layers or lenses with obscure stratification. They have slight porosity and fine-grained texture with xenoblastic grains of irregular form, which are filled with dust-like inclusions. Relict structure is commonly evident, and the fauna ordinarily remains in the form of molds (Chilingar, 1956).

C. Epigenetic Dolomites

The epigenetic dolomites result from alteration of completely lithified limestones by downward percolating meteoric solutions or rising hydrothermal solutions. Epigenetic dolomites are cavernous, having obscure stratification, patchy distribution, non-uniform grain size, and relict structure. Chilingar (1956) noted "that the Ca/Mg ratio of epigenetic dolomites varies widely over short distances, both vertically and horizontally."

Dolomitization and Porosity

At least four or five major theories have been advanced to explain the presence of significant porosity in dolomites. The classic theory, proposed by Elie de Beaumont

(1836) stated that molecular replacement of limestone by dolomite would result in a volume shrinkage of between 12 and 13 per cent. This theory ceased to receive serious consideration after 1912 when Lindgren in his well known paper on replacement pointed out that "replacement is on a volume for volume, and not molecule for molecule, basis" (Lindgren, 1912). Steidtmann (1917) described field evidence for replacement of limestone by dolomite with volume change.

The most detailed attack on the Beaumont theory was made by Murray (1930). He called attention to the fact that "the presence of oil in porous dolomitic limestones has led many to believe that the process of dolomitization has been responsible for the development of the openings in which the oil occurs." "The theory that the dolomitization of a limestone produced porosity appeared in the literature early in the 19th century. The evidence, if such there was, which gave it support seems to have been lost while the theory itself lingers. The writer was unable to find in the literature any criterion by which porosity by dolomitization can be distinguished from primary porosity or porosity developed by leaching and solution. Many dolomites are described in which the porosity is supposed to have been caused by this process, but no observer, as far as can be determined, has ever advanced any evidence in favor of this conclusion" (Murray, 1930).

The theory that the cavities in porous dolomite are produced by differential leaching of carbonate rocks has a number of adherents. There are three divisions to this theory, depending upon whether the material leached is calcite, dolomite, or fossils. The concept of the formation of cavities through the leaching of calcite is a by-product of one of the theories of the origin of dolomite advanced by Hardman (1875-77). According to this idea, the original carbonate rock was a mixture of calcite and dolomite crystals which became dolomite through the solution and removal of the more soluble calcite. "Such selective solution would produce cavities, but not local dolomitization porosity, for the non-dolomitized parts of the carbonate rock are not rich enough in dolomite crystals" (Landes, 1946).

The unusual idea that the leaching of some of the dolomite from a dolomitic limestone ooze has produced porosity was expressed by R. H. Fash (Van Tuyl, 1945).

The vulnerability of dolomite-enclosed fossil shells, especially where calcitic, to leaching by ground waters is well known (Hatch, Rastall and Black, 1938). The result of this differential leaching is a highly porous rock in the zone of weathering.

Dolomites, in addition to becoming porous through the dissolving of fossils, can become porous, and even cavernous, through ground-water solution in the same manner as limestones. Murray (1930) and Howard and David (1936) pointed out the importance of ground water leaching of carbonate rocks above the water table. Davis (1930) and (Rich 1938) emphasized the possibilities of solution below the water table, either by free or confined water.

Then, there is the theory that dolomite porosity is produced by recrystallization. This was Orton's conclusion (1888) for the porous Trenton dolomite in Ohio. J. E. Adams (1934) believed that: "Recrystallization may also be responsible for some enlargement of porosity and increase of permeability." "It is especially noted in dolomites, but may also be present in limestones" (Adams, 1934).

K. K. Landes (1946) believed "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 dolomites 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."

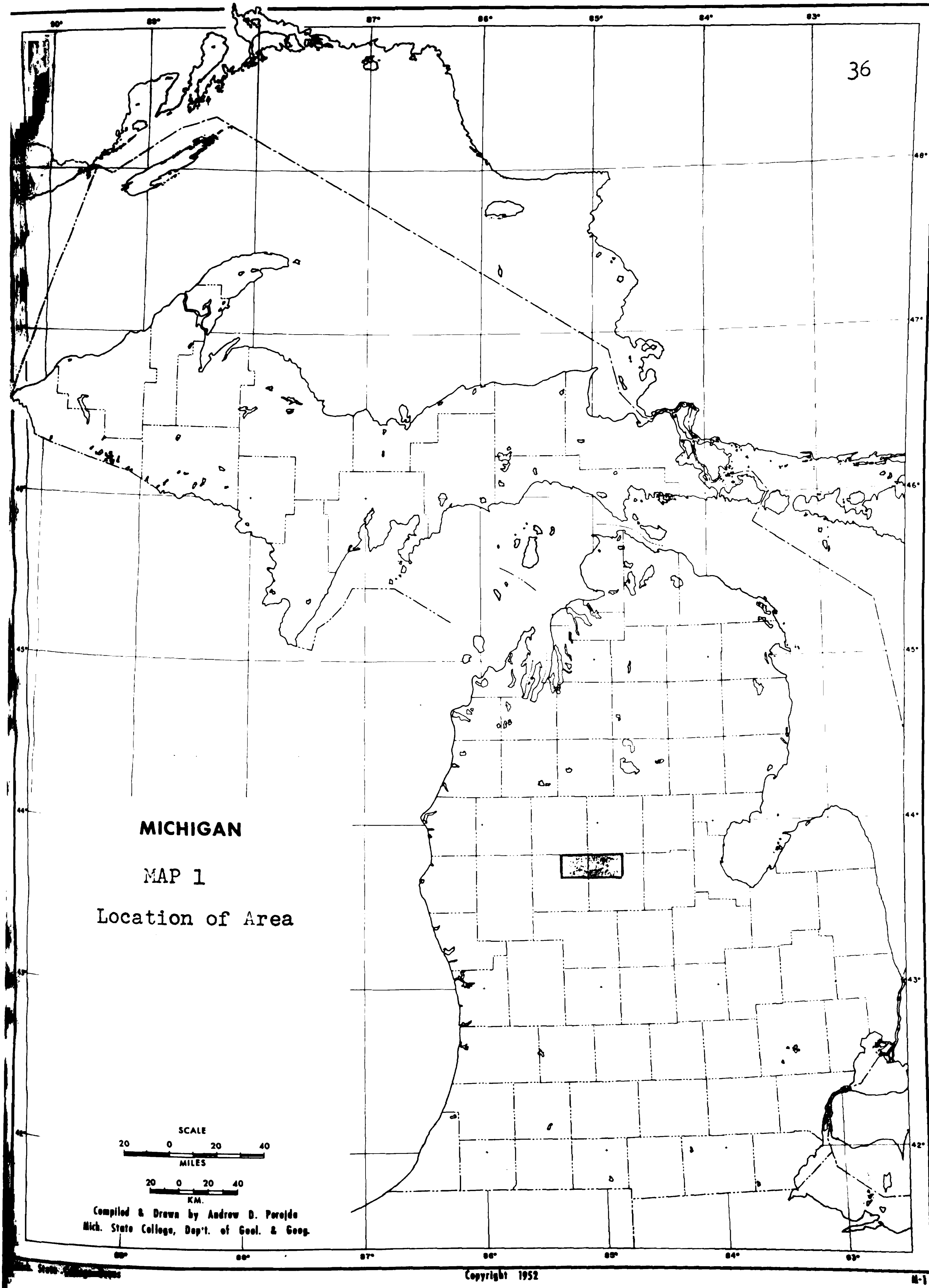
R. B. Hohlt's statement (1948) adequately concludes this review: "Because of the great amount of commercial porosity, which is restricted to dolomitic facies within limestones, there has been a growing tendency for geologists to relate porosity to the process of dolomitization." "A relationship exists between porosity and the process, or processes of dolomitization but what the specific relationships are have not been established" (Hohlt, 1948).

FIELD DATA

Location of Area

The area selected for the purpose of determining the relationships between subsurface structure and the degree of dolomitization, as reflected primarily by the Mg/Ca (Magnesium/Calcium) ratio, centers about Michigan's most prolific structural-type Rogers City fields. It consists of the northwest part of Isabella County, including Nottawa (T.15 N., R.5 W.), Sherman (T.15 N., R.6 W.), Vernon (T.16 N., R.4 W.), Gilmore (T.16 N., R.5 W.), and Coldwater (T.16 N., R.6 W.) townships, and the northeast part of Mecosta County, including Sheridan (T.15 N., R.7 W.), Martiny (T.15 N., R.8 W.), Colfax (T.15 N., R.9 W.), Fork (T. 16 N., R.7 W.) and Chippewa (T.16 N., R.8 W.) townships. The area, approximately 400 square miles, lies in the center of the Michigan basin. (See Map 1.)

Seventy wells were chosen at random from the tract studied with the availability of well samples as a restricting factor to selection. Twenty-five wells were taken from the Coldwater field exclusively for a more detailed study as related to a definite prolific structure. A total of ninety-five wells were used to represent the area for Mg/Ca ratio studies.



MICHIGAN

MAP 1

Location of Area

Oil fields producing from locally dolomitized limestones of the Rogers City formation are the Coldwater, Sherman, and Fork fields which lie on a northwest-southeast structural trend through the central portion of the area chosen for study. (See Map 2.) These fields were named by Carl C. Addison as typical examples of oil fields producing from locally dolomitized limestones (Landes, 1946).

Stratigraphy

The reservoir rock in the area of study is the Rogers City limestone of Middle Devonian age. It is overlain by the Bell Shale member of the Traverse group and lies apparently conformable with the Dundee formation. (See Figure 1.) Before the Rogers City limestone was named (Ehlers and Radabaugh, 1938) these rocks were placed in the upper-most Dundee formation and still are so classified in oil-field terminology. In some areas the formations are colloquially designated as "Dundee" or "brown lime" for the Rogers City formation, and "Dundee Restricted" or "black lime" for the lower, or true Dundee formation. In this report the formations will be referred to as the Rogers City for the upper formation and Dundee for the lower formation.

The Dundee consists of a "typical buff to light brown cherty limestone, dolomitic limestone, and dolomite varying from approximately 50 to 400 feet thick. Excepting the southeastern part of Michigan where the Rogers City is absent, the Dundee is divided into two formations. The

MICHIGAN DEVONIAN SYSTEM

System	Group	Formation
DEVONIAN	TRAVERSE	Squaw Bay
		Thunder Bay
		Potter Farm
		Norway Point
		Four Mile Dam
		Alpena
		Newton Creek
		Genshaw
		Ferron Point
		Rockport Quarry
		Bell Shale
	CAZENOVIA	Rogers City
		Dundee
	DETROIT RIVER	Lucas
		Amherstberg
		Flat Rock
		Sylvania
		Bois Blanc
		Garden Island

Figure 1. Generalized columnar section of Devonian system in Michigan basin, after Helen M. Martin, Michigan Geological Survey.

Rogers City is a typical dark-colored brownish-buff dolomitic limestone or dolomite" (Cohee, etc., 1948). It is a predominantly fossiliferous, marine limestone altered locally to dolomite in west-central Michigan and overlaps the Dundee over the northern two-thirds of the Southern Peninsula.

"The underlying Dundee formation restricted, consists typically of buff and light brown limestone, becoming more dolomitic and even containing some anhydrite in the lower part in western Michigan" (Cohee, etc., 1948). The Dundee in the east and northeastern areas of the Michigan basin is a marine limestone, predominantly tan, containing oolites and stylolites and with a more varied fauna in the peripheral areas (Knapp, 1956). "In west-central Michigan, in a belt extending north and south, a so-called 'primary' dolomite, crystalline, even-textured, predominantly tan and lacking in recognizable fossils except for occassional stromatoporoids" makes up the characteristic lithology of the Dundee (Knapp, 1956).

It is the contention of some geologists that an unconformity exists at the base of the Traverse group between the Bell shale and the Rogers City formation. R. B. Newcombe (1930) states that "the facts strongly indicate that there is a surface of unconformity at the base of the Traverse over a large part of southern Michigan, but it has not yet been clearly established." Ehlers, working in

Presque Isle County, Michigan, states that "the contact of the Rogers City limestone with the overlying Bell shale is disconformable; the effects of erosion of the Rogers City limestone prior to the deposition of the Bell shale are well illustrated" (Ehlers and Radabaugh, 1938).

K. K. Landes (1951) also states "that emergence followed the deposition of Dundee and Rogers City strata and subsequent erosion stripped these rocks from the southwestern corner of Michigan and again exposed the Detroit River group at the surface."

T. S. Knapp (1947), on the other hand, states that it is not unusual to find evidence of erosion perpheral to a deposition basin but that cores of the Bell shale-Rogers City contact "show no visible plane of demarkation between the two formations; evidence of erosion is absolutely lacking." "Therefore, in the absence of any reported direct evidence from cores of post-Rogers City erosion in the central basin area, it is apparent that the Rogers City was not eroded on any regional scale. If erosion has occurred it has been limited to isolated 'islands' which may or may not have protruded above the surface of the sea. Cores from anticlinal structures; such as are occupied by the Reed City, Coldwater, and Fork oil pools, show continuous deposition from Rogers City into Bell, so present anticlines were not necessarily sites of emergence at that time" (Knapp, 1947).

Coldwater Oil Field

The Coldwater oil field is located in the southwest quarter of Coldwater township (T.16 N., R.6 W.), Isabella County, Michigan. It is approximately 10 miles north and 14 miles west of the city of Mt. Pleasant in the west central part of the Michigan basin.

The Coldwater oil field was discovered in August, 1944. The discovery well flowed 200 barrels of oil the first 24 hours from the Rogers City dolomite. The top of the "pay" in the Rogers City lies, in most wells, within 20 feet of the base of the overlying Bell shale.

"A total of eighty-one producing wells and nine dry holes have been drilled with development substantially completed by the end of 1946. Subsequent to 1946, seven producing wells and two dry holes were drilled on the extreme edges of the field. By 1952 the cumulative production was 12,763,000 barrels of oil and 28,800,000 barrels of water and there were 69 producing wells" (Criss and McCormick, 1953).

The regional dip is northeast and the steepest dips of the Coldwater structure are along the northeast side of the field with slightly lesser dips toward synclinal reentrants along the north and south sides of the field. The major axis runs NW-SE and a minor axis trends NE-SW. (See Map 2.)

The Rogers City is a secondary dolomite 30 to 35 feet thick in the Coldwater field; the Dundee is primary dolomite 200 feet thick (Criss and McCormick, 1953). "Cores taken from two wells indicated no barrier to vertical fluid movement at the Dundee-Rogers City contact. Penetration of the Rogers City zone averaged 11 feet" (Criss and McCormick, 1953).

LABORATORY PROCEDURE

Methods

Conventional chemical methods of determining magnesium and calcium content of limestones and dolomites are time consuming and tedious, with chemical methods involving precipitation and separation of the two constituents in solution; whereas, staining methods using silver chromate, potassium ferricyanide or Lemberg's solution usually require the preparation of polished thin sections and detailed examination to determine the amounts of dolomite and calcite present (Keller, 1937; Douglas, 1944; and Clark, 1924). Spectrochemical and spectrographic analyses, although conducted with greater speed and at a low cost of operation, appear to vary in accuracy from 1.5 to 10 per cent error within a single set of data (Sloss, 1946; Anderson, 1954; Ahrens, 1950).

G. Schwarzenbach (1946) and co-workers published in Helvetica Chimica Acta a new simple titration for the determination of water hardness.[1] This method consists of the

---

[1] The "theoretical hardness of water is the sum of the concentrations of all the metallic cations other than cations of the alkali metals, expressed as equivalent calcium carbonate concentration. In most waters, nearly all of the hardness is due to calcium ion and magnesium ion. . . ." (Standard Methods, 1955).

use of ethylenediaminetetraacetic acid (commonly called versene or abbreviated EDTA) as a titrant for the sum of calcium and magnesium in water, using the dye known as Chrome Black T as an indicator.

Schwarzenback (1947) applied this method of titration to the analysis of alkaline earths and other metals. Later, Botha and Webb (1952) used this same method for the determination of calcium and magnesium in mineralized waters containing large concentrations of interfering ions. In the same year Cheng, Kurtz and Bray (1952) adapted this method to the determination of calcium, magnesium and iron in limestones without the tedious separation of the three elemenets before analysis.

In an attempt to find the most recent modifications in the improvement of this method the author reverted back to the object of its original purpose--analysis of water hardness. In the latest edition of Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, (1955) published by the American Public Health Association, several "Compleximetric" or EDTA titration methods, modified from the original procedure for more accurate results, are given for: (1) the determination of total hardness of water (the sum of Ca and Mg ions) and, (2) for the determination of Ca ion content in the presence of Mg ions using ammonium purpurate as the indicator.

The second method, as listed above, is recommended for the most accurate results (accurate to 5 parts per one million or an error of plus or minus .005 per cent) and with the advantage of analyzing for calcium in the presence of magnesium (Standard Methods, 1955).

A photometric method was adopted by the author for the determination of magnesium with an accuracy of plus or minus 1 per cent error and with the advantage of analyzing in the presence of calcium salts, directly on the water sample (Standard Methods, 1955).

The Phenanthroline-photometric method was used for the determination of the iron content with an accuracy of plus or minus 1 per cent error (Standard Methods, 1955).

The three methods used in the chemical analyses for calcium, magnesium and iron content of the limestone samples will be described here briefly since the procedure for each method is clearly outlined, step by step, in the Standard Methods manual.

Samples

Source

Cable tool and rotary tool samples were used for analysis. Cable tool samples are quite satisfactory for use and unless the sample is very fine-grained a representative portion can be selected megascopically. Samples obtained by rotary tool methods are more difficult to work with due to the necessary separation of foreign material from the rock to be analyzed. The separation procedure used by the writer was as follows: (1) every "mixed" sample was sieved, separating that portion between Tyler screens #20 and #38 (0.58-0.83mm) which corresponds to Wentworth's size classification of "coarse sand," (2) each sample was examined by means of a binocular microscope with pieces of caving removed (shale has a tendency to cave into return mud fluid, but it can be easily picked out).

Regarding rotary well samples, R. M. Whiteside (1932) states: "A sample of rotary cuttings containing less than 20 per cent of cavings or re-circulated material is considered as good workable quality." It is the opinion of the writer that there was considerably less than 20 per cent cavings in the "mixed" rotary samples.

Sample Selection

Samples which represented the top 20 feet of the Rogers City formation beneath the contact of the Bell shale were taken from each well. In the case of some wells 3 or 4 samples, taken at 5-7 foot intervals, were necessary to represent the top twenty feet. Some wells were not represented by samples for the entire 20 foot section, but whatever samples were available were analyzed. Each well was assigned a number and the samples from that well were assigned a letter, for example: Well #6, samples: 6a, 6b, 6c, and 6d.

Sample Preparation

All samples were thoroughly washed with distilled water. Agitation by shaking and decantation of the wash water aided in removing rock dust or rotary mud adhering to the particles. Shale cavings and other foreign material were removed and all "junk" iron present was picked out by passing a magnet through the sample. Each sample was then thoroughly dried over a hot plate within a closed hood.

Samples of 1.00 gram were weighed and placed in 250 milliliter beakers (Banewicz and Kenner, 1952). Ten milliliters of hydrochloric acid (1:1) and 15 milliliters of distilled water were added to each of the samples. This was evaporated to dryness, baked for approximately one hour, and allowed to cool. The residue was taken up with 3 milliliters of hydrochloric acid (1:1) and 10 milliliters of distilled water. Each solution was then filtered, washed, and made up to 200 milliliters with distilled water. The samples were now ready for the chemical analyses.

Calcium Determination

EDTA Titration Method[1]

Reagents

1. EDTA titrant. Dissolve 48 grams of disodium dihydrogen ethylenediaminetetra acetate dihydrate

---

[1] Standard Methods for the Examination of Water, Sewage, and Industrial Wastes (New York: Am. Pub. Health Assoc., 1955), p. 118.

in 9600 milliliters of distilled water. Add 10.32 grams of NaOH. Standardize this solution against a standard calcium solution by titrating 1 milliliter of the standard calcium solution with EDTA titrant in the manner described under Calculations.

2. Standard calcium solution. Dissolve 1.00 gram of reagent-grade calcium carbonate in dilute HCl, add 200 milliliters of distilled water and boil for a few minutes to expel CO_2. Cool and make up to 1 liter with distilled water in a volumetric flask. This standard contains 1.000 milligram $CaCO_3$ equivalent in each milliliter.

3. Indicator mixture. Ammonium purpurate (murexide) is used as the indicator.[1] Suspend 50 milligrams of ammonium purpurate in 50 milliliters of absolute ethyl alcohol. Store in a dropper bottle and shake before using. The suspension is stable for at least a year.

4. Sodium hydroxide solution. Dissolve 80 grams of NaOH in 800 milliliters of distilled water; cool; and dilute to 1 liter.

Essential Apparatus

1	10 ml. microburette--graduated at 0.05 ml intervals
1	1 ml pipette
1	10 ml pipette
1	50 ml pipette
2	250 ml. Erlenmeyer flasks

Procedure

1. Pipette a 1 milliliter aliquot of the dilute sample (1:200) into a 250 milliliter Erlenmeyer flask. Add 50 milliliters of distilled water.

2. Add 1 milliliter of the sodium hydroxide solution and approximately 5 drops of ammonium purpurate indicator.

3. Stir the solution and titrate with the standardized EDTA titrant. The end point is reached

---

[1] Eastman No. 6373 has been found satisfactory.

when the color of the solution changes from pink to purple.[1] (The use of an electric stirrer during titration kept the solution uniformly mixed, thus increasing the accuracy of determining the end point.) The color change at the end point is very subtle and requires some practice on the part of the analyst. Check the end point by adding 1 or 2 more drops of titrant; no further color change should occur. The titration must be completed within 5 minutes from the time of adding the NaOH.

4. Two determinations were made for each sample. The readings were within 0.05 milliliters of each other. The average of the two readings was used.

Standardization of EDTA titrant with standard calcium solution

The standard calcium solution prepared contains 1.00 milligram of $CaCO_3$ per milliliter of solution. Nine and five-hundreds (9.05) milliliters of EDTA titrant were necessary to titrate, to the end point 10 milliliters of the standard calcium solution diluted with 50 milliliters of distilled water. Titrating a distilled water blank, 0.05 milliliters of titrant were used. The amount of titrant used on the standard $CaCO_3$ solution then was 9.05 - 0.05 = 9.00 milliliters.

EDTA titrant = 10 mg $CaCO_3$ per 9.00 ml
= 1.111 mg $CaCO_3$ per 1 ml

---

[1] Ethylenediaminetetraacetic acid and its sodium salts form chelate complexes with metal cations. The calcium and magnesium complexes are colorless and the calcium-EDTA complex is more stable than the magnesium-EDTA complex. EDTA titrant combines with calcium before it combines with magnesium. At a pH of about 12 ammonium purpurate has a purple color. In the presence of traces of calcium its color turns to pink. EDTA is capable of extracting calcium from its purpurate complex and, thus, of restoring the purple color of ammonium purpurate. Magnesium does not change at this pH. These facts permit the titration of calcium in the presence of magnesium (Standard Methods, 1955, p. 113).

Calculations

Calcium as mg/liter $CaCO_3$

$$= \frac{\text{ml of titrant} \times 1{,}000 \times 1.111}{\text{ml of sample}}$$

$$= \frac{9.00 \text{ ml} \times 1{,}000 \times 1.111}{10 \text{ ml standard } CaCO_3}$$

$$= 999.99 \text{ mg/ liter } CaCO_3$$

Calcium as mg/ liter Ca

$$\text{Equivalent Wt. of Calcium} = \frac{\text{Molecular Wt. Ca}}{\text{Molecular Wt. } CaCO_3}$$

$$\text{Equivalent Wt. of Calcium} = \frac{40.08}{100.09} = .4004$$

$$= \frac{\begin{array}{c}\text{ml of}\\ \text{titrant}\end{array} \times \begin{array}{c}\text{equivalent}\\ \text{wt. of Ca}\end{array} \times \text{Volume} \times \begin{array}{c}\text{mg equivalent wt.}\\ \text{of } CaCO_3 \text{ / ml titrant}\end{array}}{\text{ml of sample used}}$$

$$= \frac{\text{ml of titrant} \times .4004 \times 1000 \times 1.111}{\text{ml sample}}$$

$$= \frac{9.00 \text{ ml} \times .4004 \times 1000 \times 1.111}{10 \text{ ml}}$$

$= 400.395$ ml/lit Ca or .4004 mg/ml Ca

Then 1 ml of titrant = .4004 mg Ca
Using 1 g of sample diluted to 200 milliliters
then $1 \text{ ml} = \frac{1 \text{ g}}{200 \text{ ml}} = .005$ g of sample

Computation of per cent calcium

If these procedures were followed in the analysis of a 1 ml portion of a 1 g sample diluted to 200 ml and 3.70 ml of titrant were used in the titration, then:

1. ml titrant x .4004 mg Ca/ml x volume = mg Ca/ml

$3.70 \times .4004 \times 1 \text{ ml} = 1.4813$ mg Ca/ml

$1.4813 \text{ mg} = .0014813 \text{ g}$

2. g of sample used : 100% :: g Ca : % Ca

.005 g : 100% :: .0014813 g Ca : % Ca

% Ca = 29.63

Magnesium Determination

Two methods for the determination of magnesium are given in the manual of Standard Methods applicable to all natural waters. Magnesium can be determined by the gravimetric method only after prior removal of calcium salts. It can, however, be determined in the presence of calcium salts, directly on the water sample by the "Photometric method." Both methods are applicable to all concentrations by the selection of suitable aliquots (Standard Methods, 1955). The method used is largely a matter of personal preference, but since it is unnecessary to separate the calcium from the magnesium before the analysis of the sample in the "Photometric method" this was adopted by the author.

Photometric Method[1]

Principle When magnesium hydroxide is precipitated in the presence of brilliant yellow, the dye is absorbed on the precipitate and its color changes from orange to bright red. A stabilizer is added to maintain the $Mg(OH)_2$ in colloidal suspension.

Interference Interference from calcium and aluminum is avoided by raising the concentrations of these ions to a level where their influence is constant and predictable.

---

[1] Standard Methods, 1955, p. 135.

Essential Apparatus

1	Spectrophotometer (Bausch and Lomb Spectronic 20), used at 525 millimicrons, providing a light path of 2.5 cm.
8	100 ml volumetric flasks
2	1 ml pipette
1	4 ml pipette
2	5 ml pipette
2	20 ml pipette

Reagents

1. Standard magnesium stock solution.[1] Add 1.000 gram of rough turnings of pure magnesium metal, not less than 99.9 per cent Mg, to a 500 ml Erlenmeyer flask. Add 150 milliliters of distilled water and 5.0 milliliters of sulfuric acid (1:1). Mix well, allow reaction to subside and boil 10 minutes. Cool; transfer to a 1 liter volumetric flask and make up to the mark. The solution should be water-white and crystal clear. 1 ml = 1.000 mg Mg

2. Standard magnesium working solution. Dilute 100.0 ml of standard magnesium stock solution to 1 liter with distilled water. This solution is equivalent to 100 mg/ liter Mg.

3. Aluminum solution. Dissolve 0.31 g $Al_2(SO_4)_3 \cdot 18H_2O$ in distilled water and dilute to 1 liter.

4. Saturated calcium sulfate solution. Saturate distilled water with $CaSO_4$ and filter.

5. Brilliant yellow solution. Dissolve 0.50 gram of solid dye (National Aniline Co., Color index No. 364 or equivalent) in liter of distilled water. Prepare freshly every 2 or 3 days.

6. Sulfuric acid solution. Add 0.3 milliliters concentrated H_2SO_4 to 1 liter of distilled water.

7. Sodium hydroxide solution. Dissolve 200 grams of NaOH in distilled water; cool; dilute to 1 liter.

---

[1] High purity magnesium is available from Dominion Magnesium Ltd., Suite 1505, 320 Bay Street, Toronto, Ont., Canada.

8. Stabilizing solution-Colloresin LV. Suspend 1.00 gram of Colloresin LV in 100 ml of distilled water by shaking. Place in a refrigerator overnight, and allow to reach the same temperature of other reagents before use.

9. Sodium sulfite solution. Dissolve 1.0 gram of anhydrous Na_2SO_3 in 100 ml distilled water. Prepare freshly each day.

Procedure

1. Pipette 1 ml of diluted sample (1:200) into a 100 ml volumetric flask (if sample is further diluted 20 ml are used).

2. Add 1 ml of sodium sulfite solution.

3. Add, in order, 1 ml H_2SO_4 solution, 20 ml calcium sulfate solution, and 5.0 ml aluminum solution.

4. Bring volume to about 80 ml with distilled water and mix.

5. Add 5.0 ml of Colloresin LV, 2.0 ml of brilliant yellow solution, and 4.0 ml NaOH solution.

6. Dilute to the mark; shake vigorously; and wait 5 minutes for full color development.

7. Compare photometrically within an hour against a blank prepared from distilled water and all of the reagents. Use selected, optically matched, 1 inch test tubes and adjust the difraction grating in the spectrometer to transmit light having a wavelength of 525 mmu. Set the instrument at 100% transmittance using this blank.

Standard Calibration Curve for Magnesium

A standard curve should be drawn on single cycle semilogarithmic paper with the per cent transmittance plotted on the logarithmic axis and the concentration of magnesium plotted on the arithmetic axis. The curve should be drawn through at least 5 points corresponding to .01, .02, .04, .06, .08, and .10 grams of Mg per 100 milliliters made from the dilute standard working solution of Mg. A new curve should be prepared for each batch of reagents.[1]

Calculations

Results are read directly from the instrument in units of per cent light transmittancy through the colored sample. Referring to the standard calibration curve the concentration of the sample can be determined in grams of magnesium per 100 milliliters.

$$\% \text{ Mg} = \frac{\text{g Mg/100 ml (read from calibration curve)}}{\text{ml aliquot} \times \text{g of sample/ ml of diluted original sample}}$$

$$\% \text{ Mg} = \text{grams of Mg/100 grams of original sample}$$

Computation of Percentage Magnesium

If these procedures were followed and in the analysis of the sample (dilution 1:200) per cent light transmittancy was read as 79% from the instrument then the concentration of Mg in the sample per 100 milliliters is 0.046 g as read from the calibration curve for magnesium.

$$\% \text{ Mg} = \frac{0.046 \text{ g/100 ml}}{1 \text{ ml} \times .005 \text{ g}} = 9.20\%$$

Magnesium-Calcium Ratios

The ratio of calcium to magnesium may vary from 1.50 (in a normal dolomite) to infinity (in a pure limestone). On the other hand, the magnesium to calcium ratio will give results within well defined limits which can be readily applied to graphs and maps.

The ratio of Mg to Ca can be calculated from the relative percentages as previously determined.

---

[1] Hawk, Oser and Summerson, "Relation between transmittance and concentration," Practical Physiological Chemistry, 12th ed. (1947), p. 469.

Example:

$$\begin{array}{ll} Mg = 9.20\% & Mg/Ca = \dfrac{9.20}{29.63} = 0.310 \\ Ca = 29.63\% & \end{array}$$

(See Table I for Mg/Ca ratios.)

Iron Determination

Phenanthroline Method[1]
(A Colorimetric Method)

The Phenanthroline method has been used for many years for testing iron in a water supply and is known to be reliable, if interfering substances are absent. Known interfering ions are phosphates, chromium, copper, nickel, cobalt, zinc, mercury, silver, cadmium, bismuth, fluoride, molybdate, citrate, oxalate, tartrate, and some of the rarer metals. Complete chemical analysis of dolomites and limestones indicate none of the above named interfering ions (Pirsson and Knopf, 1949).

Essential Apparatus

1	Spectrophotometer (Bausch and Lomb Spectronic 20), for use at 510 mmu providing a light path of 1 to 10 cm.
2	1 ml pipette
2	10 ml pipette
12	100 ml volumetric flasks
1	pH meter

Note. All glassware must be acid-washed to remove iron oxide film.

Reagents

1. Hydrochloric acid. Set aside a supply of concentrated HCl for this determination. Because

---

[1] Standard Methods, 1955, p. 125.

HCl content varies from 35 to 38 per cent, the sodium acetate solution must be adjusted for the particular lot of HCl to be used.

2. Sodium acetate solution. Dissolve 350 grams of $NaC_2H_3O_2.3H_2O$ in 500 ml. of distilled water and dilute to approximately 1 liter. Using conc. HCl and a pH meter adjust the pH of this solution to a value between 3.2 and 3.3.

3. Hydroxylamine reagent. Dissolve 10 grams of $NH_2OH{\cdot}HCl$ in 100 ml of distilled water.

4. 1,10 Phenanthroline solution. Dissolve 0.12 gram $C_{12}H_8N_2.H_2O$ in 100 ml of distilled water by stirring and heating to 80°C.; do not boil.

5. Standard iron stock solution. Use electrolytic iron wire to prepare the standard. Dissolve 0.2000 gram of wire in 20 ml H_2SO_4(1:5) in a 1 liter volumetric flask. Dilute to mark with distilled water. This stock solution contains 200.0 mg Fe/liter.

6. Standard iron working solution. Pipette 5.0 ml standard iron stock solution into a liter volumetric flask and dilute to mark with distilled water. This contains 10.0 mg Fe/liter. Then pipette 5.0 ml into a 1 liter volumetric flask and dilute to mark with distilled water. This contains 1.0 mg Fe/liter.

Procedure

1. Add 1 ml of the dilute sample (1:200) that is to be analyzed to a 100 ml volumetric flask.

2. Add, in order, 1 ml of hydroxylamine, 10 ml of sodium acatate solution and 10 ml of 1,10 phenanthroline solution.

3. Mix thoroughly and dilute to mark.

4. Wait 15 minutes for color development.

5. Compare photometrically within an hour against a blank prepared from distilled water and all of the reagents. Use selected, optically matched, 1 inch test tubes and adjust the difraction grating to transmit light having a wavelength of 510 mmu. Set the instrument at 100% transmittance using this blank.

Standard Calibration Curve for Iron

A standard curve should be drawn on single-cycle semi-logarithmic paper with the per cent transmittance plotted on the logarithmic axis and the concentration of iron plotted on the arithmetic axis. The curve should be drawn through at least 5 points corresponding to .005, .01, .02, .03, .04, and .05 grams of Fe per 100 milliliters from the dilute Fe working solution. A new curve should be prepared for each batch of reagents.[1]

Calculations

Results are read directly from the instrument in units of per cent light transmittancy through the colored sample. Referring to the standard calibration curve the concentration of the sample can be determined in grams of iron per 100 milliliters.

$$\%\text{Fe} = \frac{\text{g Fe /100 ml (read from calibration curve)}}{\text{ml aliquot x g of sample/ ml of diluted original sample}}$$

Computation of Percentage Fe

If these procedures were followed and in the analysis of the sample (dilution 1:200) the percent transmittancy was read as 53.0% from the instrument then the concentration of Fe in the sample per 100 milliliters is 0.0129 gram as read from a calibration curve for iron.

$$\%\text{Fe} = \frac{0.0129\ \text{g/100 ml}}{1\ \text{ml x .005 g}} = 2.58\%$$

Results of Chemical Analyses

Table I records the ninety-five well locations and information along with a summary of the chemical analyses of the 250 samples for calcium, magnesium and iron. The magnesium to calcium ratios are also recorded in Table I.

---

[1] Hawk, Oser and Summerson, "Relation between transmittance and concentration," Practical Physiological Chemistry, 12th ed. (1947), p. 469.

These data were used in plotting and drafting lithologic ratio maps and for statistical interpretations which are presented in the following chapters.

TABLE 1

WELL DATA AND LOCATIONS

Permit No.	Well Name & Operator	Location	Elev.	Top of R.C.[1] Formation
16861	Fate & Weis Merrill Drilling Co.	15N-7W-27 SW-NW-SW	1078.7	3838
4137	Gingrich #1 King Drilling	15N-7W-12 W1/2-SE-SW	978.6	3769
10043	McCormack #1 Sun Oil Co.	16N-8W-23 S1/2-SE-SE	1072.3	3840
5109	Thrush #1 Daily Crude Oil	16N-7W-25 SW-NW-SE	997.4	3790
16329	A. McNeely #1 L. Rose	16N-7W-3 NW-NW-NW	1077.0	3868
4650	Robart #1 Sun Oil Co.	16N-7W-29 N1/2-NE-NW	1042.6	3815
6645	Wm. Bongard #1 Turner Petr. Co.	16N-7W-21 S1/2-NW-NE	1033.3	3821
9663	*Murray #1 Sun Oil Co.	16N-7W-5 S1/2-NW-SW	1068.3	3813
2474	Fred Siegel #1 Farwell Oil	17N-5W-26 NW-SE-SE	897.1	3888
2524	H. Fordyce #1 W. Hunter	16N-5W-34 C-NW-NE	916.0	3943
11722	*Cheadle #1 Sohio Petr. Co.	16N-6W-33 N1/2-NW-SE	970.5	3738
5242	Stevens #1 Keeler & Chatham Oil	16N-6W-13 SW-SW-NW	1030.2	3964

---

[1] Rogers City

*Producing Oil Wells

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
1	0 - 4	1.50	15.62	30.50	1.953
2a	0 - 6	1.34	22.82	13.20	0.578
2b	6 -11	0.70	25.23	11.00	0.436
3a	0 - 3	2.36	10.66	24.00	2.251
3b	3 - 7	1.54	14.98	23.00	1.535
4a	0 -15	1.48	11.62	25.25	2.173
4b	15 -20	0.80	12.42	37.00	2.979
5a	0 - 7	0.90	14.18	27.50	1.939
5b	7 -10	0.64	15.38	17.50	1.138
5c	10 -14	0.50	14.82	21.00	1.417
6a	0 - 3	6.44	20.02	19.00	0.949
6b	3 - 6	2.70	12.18	23.50	1.929
6c	6 - 9	1.10	14.02	23.00	1.641
6d	9 -15	0.64	14.50	14.00	0.966
7	0 - 6	0.76	13.62	12.50	0.918
8	0 - 4	1.40	12.58	11.90	0.946
9	0 - 6	1.10	19.22	3.75	0.195
10a	6 - 8	1.20	14.98	11.50	0.768
10b	8 -13	1.06	14.18	3.00	0.212
11a	13 -21	0.90	14.02	4.60	0.328
11b	21 -26	0.58	14.58	5.50	0.377
11c	26 -33	0.48	14.58	9.47	0.650
12a	0 - 8	1.24	16.42	5.50	0.335
12b	8 -18	1.10	22.82	9.60	0.421

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R.C.[1] Formation
15964	J. R. Forbes #1 I. Hartman	16N-6W-34 SW-SE-SW	983.6	3775
15796	J. M. Schafer #1 Nottawa Oil	15N-5W-9 SE-SE-NE	906.3	3859
12088	Dent #1 Sohio Petr.Co.	15N-6W-5 N1/2-NE-NW	987.9	3740
11858	*Diehl #1 Chartiers Oil	15N-6W-29 N1/2-SW-NW	1047.6	3768
3725	Lintmuth #32 Taggart Bros.	15N-9W-35 NW-NW-NW	1092.0	3659
9608	Wood #1 C. W. Teater	15N-7W-2 N1/2-NW-NE	1020.4	3804
982	Grove #1 Benedun-Trees	15N-7W-14 NW-NW-SE	1021.0	3792
17892	Floyd Bouck #1 Rex Oil & Gas	15N-8W-11 N1/2-NW-NE	1038.0	3741
14430	Emma Smith #1 Pure Oil Co.	15N-8W-10 NW-NW-NE	1047.6	3738
11756	V. Minkel #1 Chapman Oil Co.	14N-8W-7 S1/2-SW-SW	1027.4	3628
19610	G. Snyder #1 IMO Oil Co.	14N-7W-6 SE-SE-SE	1007.6	3690
3648	Gorr #1 Chartiers Oil	16N-4W-6 SE-NE-SW	960.0	3951

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
13	0 - 8	1.68	13.38	10.50	0.785
14a	2 - 6	0.80	13.38	6.25	0.467
14b	6 - 9	0.80	13.62	13.25	0.973
14c	9 -16	0.64	15.62	9.75	0.624
14d	16 -21	0.70	14.18	10.00	0.705
15a	3 - 6	1.32	12.98	7.00	0.539
15b	6 - 9.5	1.30	13.77	7.87	0.572
16a	0 - 4.5	1.18	14.02	7.87	0.561
16b	4.5 -10.5	1.14	14.98	6.75	0.451
17a	1 - 3	1.80	19.78	4.30	0.217
17b	3 - 8	1.40	25.23	4.08	0.162
18a	0 - 7	1.26	24.98	3.80	0.152
18b	7 -15	1.72	28.59	7.16	0.250
18c	15 -23	1.34	26.19	4.60	0.176
19a	3 - 8	2.60	17.78	1.60	0.090
19b	8 -10	2.90	17.62	1.40	0.079
19c	10 -14	1.84	24.82	2.28	0.095
19d	14 -20	1.84	23.78	11.40	0.479
20	0 - 7	2.96	12.01	21.00	1.749
21a	0 - 4	4.16	14.98	21.62	1.443
21b	4 -10	2.86	24.42	20.40	0.835
21c	10 -18	1.80	22.98	5.00	0.218
22a	0 -10	4.70	13.21	5.87	0.444
22b	10 -20	3.70	12.41	3.75	0.302
23a	4 - 8	3.28	8.97	6.00	0.669
23b	8 -14	2.30	11.77	4.55	0.387
23c	14 -19	1.78	6.17	3.00	0.486
24	0 - 1	0.30	24.58	4.34	0.177

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R.C.[1] Formation
17389	D. Knox #1 J. W. Sturman	17N-6W-35 SE-SE-SE	1087.7	4055
2601	Davy & McLachlan #1-Sun Oil Co.	17N-8W-35 C-NW-NW	1106.0	3911
16335	Lloyd #1 Roosevelt Oil	17N-7W-34 NW-NW-SW	1038.5	3795
16139	State-Garfield #1-Sam Hindman	17N-6W-33 E1/2-NW-NE	1074.0	3956
16938	Frank Smith #1 I. Hartman	16N-7W-4 NW-NW-NE	1055.1	3818
15437	Williams #1 J. E. Bauer	16N-7W-24 NW-NW-NW	1073.3	3886
19195	J. Stockwell #1 McClure Oil	16N-8W-22 NE-NE-SE	1086.1	3854
17277	D. Church "B"#1 Sun Oil Co.	16N-8W-2 S1/2-NE-NW	1188.2	3959
17151	Sparks #1 Chapman Oil	16N-8W-15 NE-SE-SE	1143.0	3905
15606	Brewer-Smith #1 Sohio Oil Co.	16N-8W-35 NE-NW-SW	1015.5	3771
3428	Waters #1 Taggart & Rowe	16N-8W-28 NW-SW-SE	1100.0	3855

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
25a	0 -10	0.56	20.18	3.64	0.180
25b	10 -16	0.56	20.98	5.90	0.281
26a	0 - 7	0.50	22.18	9.60	0.433
26b	7 -12	0.46	27.39	10.60	0.387
27a	0 - 2	1.30	11.77	4.83	0.410
27b	2 - 5	1.56	13.38	4.13	0.308
27c	5 - 7	0.60	13.62	7.38	0.541
27d	7 - 9	0.68	14.41	2.85	0.198
28a	0 - 4.5	2.00	10.81	7.70	0.712
28b	4.5 - 7.5	1.32	12.98	7.88	0.607
28c	7.5 -12.5	0.86	14.41	10.75	0.746
28d	12.5 -37.0	0.80	14.58	6.00	0.412
29a	0 - 6	1.46	13.21	6.75	0.511
29b	6 - 9	1.70	12.81	2.30	0.180
29c	9 -13	1.00	13.77	4.20	0.305
30a	0 - 3	5.50	12.98	2.30	0.177
30b	3 - 8	2.18	13.62	11.25	0.826
30c	8 -13	1.68	14.58	10.50	0.720
31a	4 - 8	0.80	13.77	9.17	0.666
31b	8 -13	0.82	13.38	3.50	0.262
32a	0 - 3	2.10	10.17	2.30	0.226
32b	3 - 4	1.20	10.17	2.30	0.226
32c	13 -14	0.64	23.62	10.60	0.449
33a	0 -10	2.50	9.77	15.80	1.617
33b	10 -11	1.90	11.62	21.80	1.876
33c	11 -14	1.20	14.02	4.08	0.291
33d	14 -19	0.86	12.58	4.50	0.358
34a	0 - 5	2.24	14.41	5.88	0.408
34b	5 -10	1.60	14.02	3.25	0.232
35a	0 - 8	1.96	13.38	6.50	0.486
35b	8 -17	1.10	20.02	7.50	0.375
35c	17 -24	0.80	22.58	13.75	0.609

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R.C. Formation
16577	Lake Prop.,#1 Collin & Walton	16N-7W-36 NE-NW-NW	950.7	3736
12725	L. Harper #1 Sun Oil Co.	16N-7W-31 N1/2-SW-NE	1094.0	3846
19283	Ralph Unit #1 Gulf Refining Co.	16N-7W-8 NE-SW-NW	1079.2	3812
3357	Hoffman #1 Daily Crude Oil	16N-7W-9 NW-SW-SE	1029.7	3793
3516	Cook #1 McClanahan Oil	16N-5W-15 NW-NW-SE	928.0	4005
1235	Wilson #1 F. L. Maire	16N-5W-12 NE-SE-NE	945.0	3995
12635	Gamble #1 J. V. Wickland	16N-5W-23 NW-NW-NE	924.0	3970
19287	G. Hamilton #1 Neyer et al.	16N-5W-19 NW-SW-SE	983.3	3887
19394	Powell #3 Neyer et al.	16N-5W-30 SE-SE-NE	913.9	3802
19050	Powell #2 J. Neyer	16N-5W-30 NW-SW-NE	971.5	3870

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
36a	0 - 5	1.90	19.62	3.00	0.153
36b	5 -10	1.00	21.78	6.00	0.275
36c	10 -15	1.36	22.82	4.30	0.188
36d	15 -20	1.20	22.98	2.76	0.120
37a	0 - 5	2.06	18.58	3.40	0.183
37b	5 -11	0.98	23.22	3.30	0.142
37c	11 -17	0.50	24.18	7.16	0.296
37d	17.-26	0.64	24.98	5.74	0.230
38a	0 - 5	3.00	4.16	4.40	1.058
38b	5 -10	1.20	12.81	4.55	0.355
38c	10 -15	1.24	14.02	10.00	0.713
38d	15 -20	2.66	8.01	6.00	0.749
39a	0 - 8	2.16	4.96	4.40	0.887
39b	8 -13	0.80	13.85	3.75	0.271
39c	13 -19	0.70	14.98	4.13	0.275
40a	0 - 4	1.72	16.82	2.00	0.119
40b	4 -12	1.70	18.98	2.00	0.105
40c	12 -17	1.14	21.22	4.60	0.217
41a	0 - 5	2.44	18.18	4.83	0.265
41b	5 - 8	1.50	21.38	9.60	0.449
41c	8 -11	0.80	22.02	9.40	0.427
41d	11 -13	1.10	30.99	1.40	0.045
42a	0 - 5	1.24	18.58	3.86	0.208
42b	5 - 9	1.04	21.38	2.60	0.122
42c	9 -15	0.68	23.22	5.40	0.233
42d	15 -20	0.76	24.18	3.00	0.124
43a	0 - 6	1.50	12.58	2.00	0.159
43b	6 -12	0.92	14.18	2.63	0.185
44a	0 - 2	2.00	9.37	4.00	0.427
44b	2 - 4	1.90	9.21	3.45	0.375
45a	0 - 6	2.00	12.01	8.95	0.745
45b	8 -10	8.50	12.42	5.10	0.411
45c	10 -13	5.28	14.41	8.13	0.564
45d	13 -20	1.50	15.38	5.10	0.332

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R. C. Formation
18645	Powell #1 J. Neyer	16N-5W-30 N1/2-NE-NE	944.9	3835
12512	E. Maybee #1 Merrill Drlg.Co.	15N-5W-12 NE-SE-SE	837.8	3770
12779	Frank Bowee #1 Collin & Walton	15N-5W-23 SE-NE-SE	837.5	3767
3706	Hicks #1 M. Smith	15N-6W-35 SW-SW-NW	915.4	3640
12956	Carr #1 Bell & ATHA	15N-6W-25 NW-NW-SW	906.0	3688
19606	J. & M. Vogel #1 Merrill Drlg.Co.	15N-5W-10 NE-NE-NE	900.3	3856
6038	Tillman #1 Teater	15N-5W-23 NE-SE-NW	855.7	3821
15781	L. Huber #1 Basin Oil Co.	15N-5W-36 NW-SE-NE	832.0	3725
19865	Grewerre & Cliff Est. #1 Leonard Oil	15N-5W-19 SE-NW-NW	884.1	3693
5453	Hauck #1 Gulf Ref. Co.	15N-5W-13 SW-NW-SW	850.0	3791

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
46a	0 - 2	1.90	11.21	7.50	0.669
46b	2 - 4	2.90	10.81	7.50	0.694
46c	4 - 5	2.58	11.21	2.20	0.196
47a	0 - 4	3.66	14.02	5.10	0.364
47b	4 - 9	4.50	14.41	1.50	0.104
47c	9 -12	1.34	14.58	3.45	0.237
48a	6 -11	0.74	14.41	5.10	0.354
48b	11 -14	0.60	14.82	1.50	0.101
48c	14 -18	0.01	13.77	2.20	0.160
49a	0 - 5	0.76	14.18	1.75	0.123
49b	5 - 9	0.74	14.02	1.60	0.114
49c	9 -13	0.48	14.82	1.75	0.118
49d	13 -17	0.30	14.41	5.40	0.375
50a	0 - 5	0.70	12.17	1.84	0.151
50b	5 -12	0.92	10.01	1.50	0.150
50c	12 -19	0.68	12.98	3.75	0.289
50d	19 -24	1.40	10.01	1.28	0.128
51a	0 - 5	0.70	12.81	11.70	0.913
51b	5 -10	0.56	13.62	8.40	0.617
52a	0 - 3.5	1.62	11.62	6.16	0.530
52b	3.5 -12.5	0.64	13.62	11.10	0.814
52c	12.5 -17.5	0.80	13.21	5.40	0.409
53a	0 - 6	1.14	11.21	5.60	0.500
53b	6 -11	1.04	12.58	5.60	0.445
53c	11 -18	0.94	14.18	5.40	0.381
54a	0 - 5	0.94	14.58	5.60	0.384
54b	5 -10	0.82	14.82	4.00	0.270
54c	10 -13	0.70	14.82	3.00	0.202
54d	13 -18	0.66	14.18	6.00	0.423
55a	0 - 3	1.50	14.02	5.40	0.385
55b	3 - 9	0.98	14.41	6.16	0.427
55c	9 -12	1.20	14.82	8.20	0.553

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R. C. Formation
4862	*Ryckman #1 Pure Oil Co.	15N-6W-33 NW-SW-NE	1003.0	3701
4220	Lawens #4 J.V.Wickland Dev.	15N-5W-24 NW-SW-SE	838.6	3776
4255	F. Cotter #1 C. Weller	15N-5W-11 NE-NE-NE	838.0	3799
4663	McClintic B-8 Pure Oil Co.	15N-6W-35 SW-SW-SW	952.5	3653
3713	Merrihew #1 Turner Petr. Co.	15N-6W-28 SE-SE-NW	1005.2	3736
6369	*Walch #1 Borough	15N-6W-18 SW-SW-NW	996.2	3745
19842	State-Sherman "QN" -#1 Brazos Oil Co.	15N-6W-21 SE-NE-NE	925.6	3671
19265	Woodin #1 Leonard Oil Co.	16N-6W-35 NW-SW-SW	962.6	3757
17561	J. L. Bean #1 Chartiers Oil Co.	15N-6W-8 SW-NW-SW	1005.4	3775
16244	A. Dent #1 J. Neyer	15N-6W-6 N1/2-SE-SE	977.8	3731
12936	*Hatcher #1 Pure Oil Co.	15N-6W-6 N1/2-NE-SE	998.5	3754
12378	*L. B. Wilson #2 Sohio Petr. Co.	16N-6W-30 N1/2-SW-NE	1054.5	3806

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
56a	0 - 3	1.10	14.41	12.60	0.874
56b	3 - 4	0.80	14.41	11.40	0.791
56c	4 - 5	0.68	15.38	10.60	0.689
57a	0 - 3	1.06	14.82	11.40	0.769
57b	4 - 9	0.90	14.98	12.20	0.814
57c	9 -16	0.66	14.58	12.40	0.850
58a	0 - 5	4.04	9.21	3.50	0.380
58b	5 -12	3.24	10.81	10.25	0.948
58c	12 -14	1.78	13.77	11.20	0.813
59	0 - 4	0.98	14.98	12.20	0.814
60a	0 -12	2.16	10.41	10.50	1.009
60b	12 -19	1.86	9.61	7.87	0.819
61a	0 -10	2.16	16.02	5.90	0.368
61b	10 -15	2.04	17.00	3.40	0.200
62a	0 - 6	0.98	13.77	9.20	0.668
62b	6 -12	1.18	12.98	17.92	1.381
62c	12 -22	0.68	14.02	6.16	0.439
63a	0 - 1	1.86	3.20	6.00	1.875
63b	1.5 -4.5	1.96	10.81	2.20	0.204
63c	4.5 -7.5	1.90	10.17	4.76	0.468
64a	0 - 4	2.96	9.37	4.76	0.508
64b	4 -10	1.04	7.77	2.20	0.283
64c	10 -15.5	1.10	13.21	5.00	0.379
64d	15.5 -20.5	0.68	13.38	4.25	0.318
65a	6 -11	1.24	8.01	5.60	0.699
65b	11 -16	1.30	17.22	7.34	0.426
66	0 - 5	2.00	10.81	2.20	0.204
67a	0 - 7	0.80	13.77	11.20	0.813
67b	7 - 9.5	0.76	14.82	13.10	0.884
67c	9.5 -12.5	0.70	14.58	16.00	1.097

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R. C. Formation
12911	*Mina DeLong #1 Mogul Oil Co.	16N-6W-20 S1/2-SE-SE	998.1	3748
18337	M. Drallette #1 C. Glavin	15N-6W-13 NE-NW-SW	908.0	3707
10131	Gringrich #1 Gordon Oil Co.	15N-6W-7 W1/2-NW-NW	943.9	3702
4741	*Buetler #2 Pure Oil Co.	15N-6W-33 SW-NW-NE	1012.0	3710
12187	*Tower #1 Pure Oil Co.	15N-6W-5 N1/2-SE-NW	991.7	3747
12464	*O. Dague #3 Sohio Petr. Co.	16N-6W-30 N1/2-NW-SE	1021.9	3785
12681	*E. L. Chapman #2 Sohio Petr. Co.	16N-6W-30 S1/2-NW-NE	1054.8	3808
12182	*E. Chapman #1 Sohio Petr. Co.	16N-6W-30 S1/2-NE-NE	1031.9	3768
11639	*Conley #2 Sohio Petr. Co.	16N-6W-28 N1/2-NW-NE	975.0	3750
11220	*Rogers #1 Cities Service	16N-6W-29 N1/2-SW-SE	1016.5	3732
12078	*State #1 Cities Service	16N-6W-32 N1/2-SW-SE	995.0	3757
483	Anderson #1 Big Rapids Oil	15N-9W-14 NE-NE-NE	1013.0	3610

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
68a	0 - 2	2.04	10.01	14.00	1.399
68b	2 - 9	1.34	12.17	8.60	0.707
68c	10 -11	0.92	13.21	8.40	0.636
69a	0 - 4	1.50	11.37	6.16	0.542
69b	4 - 9	0.98	12.98	6.56	0.505
69c	9 -16	0.68	14.58	7.34	0.503
69d	16 -20	0.64	14.18	5.90	0.416
70a	0 - 7	0.80	23.39	9.00	0.385
70b	7 -14	0.80	21.22	8.60	0.405
70c	14 -22	0.52	23.78	4.08	0.172
71	17 -22	1.14	12.42	3.86	0.311
72a	0 - 2	2.16	11.77	5.00	0.425
72b	2 - 5	1.40	14.41	5.40	0.375
73a	0 - 4	1.18	13.62	6.30	0.463
73b	4 - 7	0.90	14.18	7.80	0.550
74a	0 - 3.5	1.60	9.37	3.00	0.320
74b	3.5 - 7.5	0.80	13.38	4.92	0.368
75a	0 - 4	0.60	14.41	5.28	0.366
75b	4 - 6	0.52	15.62	6.30	0.403
75c	6 - 9	0.60	14.82	5.90	0.398
76a	0 - 6	0.64	14.18	5.60	0.395
76b	6 - 9	0.56	13.62	6.56	0.482
76c	9 -14	0.30	9.21	4.25	0.461
76d	14 -19	0.40	14.82	5.00	0.337
77a	0 - 4	1.60	9.37	2.75	0.293
77b	4 - 7	1.32	12.42	1.84	0.148
77c	7 - 9	0.80	13.77	6.56	0.476
78a	0 - 3	1.00	12.01	3.30	0.275
78b	3 - 4.5	0.74	13.21	6.56	0.497
79	0 -20	0.98	18.58	4.92	0.265

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R. C. Formation
4075	Hutchins #1 Daily Crude Oil	15N-7W-8 NW-NW-NW	1002.2	3717
9806	Helmer #1 Gordan Oil Co.	15N-8W-17 S1/2-NE-NE	1048.2	3765
11182	*E. S. Cole #1 Sohio Petr. Co.	16N-6W-32 N1/2-SW-NE	971.6	3695
11218	*Cole #3 Sohio Petr. Co.	16N-6W-32 N1/2-NW-SE	995.5	3737
11183	*Durkee #1 Sohio Petr. Co.	16N-6W-32 N1/2-NE-NW	983.6	3704
10997	*Cummings #4 Sohio Petr. Co.	16N-6W-32 N1/2-NE-NE	974.9	3688
12087	*H. Durkee #1 Sohio Petr. Co.	16N-6W-31 N1/2-NE-SE	973.1	3726
11523	*Dague #A-1 Sohio Petr. Co.	16N-6W-31 N1/2-NE-NE	1002.2	3757
12827	*Cheadle #1 G.Hanners	16N-6W-33 N1/2-NE-SE	970.6	3744
11524	*F. Sisco #1 Sohio Petr. Co.	16N-6W-33 N1/2-NE-NE	972.5	3720
11321	*W. Sisco #1 Sohio Petr. Co.	16N-6W-33 N1/2-NW-NE	976.6	3692
11142	*Coe #1 Sohio Petr. Co.	16N-6W-33 N1/2-NW-SW	979.4	3745

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
80a	0 - 7	0.92	21.62	3.00	0.139
80b	7 -14	0.80	20.98	3.86	0.184
81	0 -20	1.14	16.02	1.60	0.100
82a	0 - 8	1.44	13.62	3.64	0.267
82b	8 -11	0.68	12.81	5.00	0.390
82c	11 -13	2.32	10.41	9.47	0.910
83a	0 - 4	1.64	13.38	11.20	0.837
83b	4 - 8	0.98	14.82	12.90	0.870
83c	8 -12	0.76	14.41	14.80	1.027
84a	0 - 3	2.98	10.17	4.92	0.484
84b	3 - 9	3.20	9.77	13.25	1.356
85a	0 - 5	1.34	12.98	12.40	0.955
85b	5 -10	1.54	13.77	12.00	0.871
85c	10 -17	1.64	12.42	11.40	0.918
86a	0 - 1	1.64	13.38	11.00	0.822
86b	1 - 6	1.00	14.18	13.52	0.953
86c	6 -13	0.64	14.58	14.30	0.981
87a	0 - 4	1.44	11.62	12.40	1.067
87b	4 - 7	0.80	14.41	13.10	0.909
88	0 - 2	0.44	15.38	12.00	0.780
89a	0 - 3	0.50	15.22	12.00	0.788
89b	3 - 6.5	0.56	14.18	11.70	0.825
90a	0 - 5	0.90	14.18	6.30	0.444
90b	5 - 9	0.98	14.02	5.00	0.357
90c	9 -14	0.46	14.18	5.28	0.372
91a	0 - 4	1.78	10.97	3.00	0.273
91b	4 - 9.5	0.74	14.41	6.56	0.455
91c	9.5 -14.5	0.52	14.58	4.60	0.316

TABLE 1--Continued

Permit No.	Well Name & Operator	Location	Elev.	Top of R. C. Formation
11337	*R. O. Dague #2 Sohio Petr. Co.	16N-6W-29 N1/2-NW-SW	1016.1	3749
11092	*Rodgers #1 Sohio Petr. Co.	16N-6W-29 N1/2-SE-SE	1002.2	3719
11446	*E. L. DeLong #1 Sohio Petr. Co.	16N-6W-29 N1/2-NE-NW	993.3	3755
11242	*Watkins #2 Sohio Petr. Co.	16N-6W-29 N1/2-SW-NE	984.1	3711

TABLE 1--Continued

Sample No.	Feet below top of R.C.	Pct. Fe	Pct. Ca	Pct. Mg	Mg/Ca Ratio
92a	0 - 6	1.44	10.97	5.60	0.510
92b	6 -12	0.88	14.41	5.90	0.409
92c	12 -17	0.60	15.38	4.08	0.265
93a	0 - 5	2.44	7.21	9.20	1.276
93b	5 - 9	0.76	13.77	6.30	0.458
93c	9 -14	0.66	13.38	5.28	0.395
94a	0 - 2	1.64	14.18	5.40	0.381
94b	2 - 3.5	1.24	14.41	4.60	0.319
95a	0 - 3	0.68	14.02	4.60	0.328
95b	3 - 6	0.80	12.81	7.16	0.559
95c	6 - 9	0.68	14.41	3.30	0.229

INTERPRETATION OF DATA

Structural and Chemical Interpretation

Structure Contour Map

A structure contour map was plotted and interpolated for all available data on the top of the Rogers City-Dundee formation for the 400 square mile area studied. The structural interpretation was based exclusively upon samples for the ninety-five wells studied; and well logs and steel line readings for all the other wells drilled in the area which penetrated the top of the Rogers City limestone, but for which there were no samples available. No interpretation for the Rogers City-Dundee was made upon data from overlying formations.

Map 2 (See pocket) is the structure contour interpretation on a scale of one inch to the mile and with a contour interval of 25 feet.

Structural Interpretation

The interpretation of the structure contour map for the area is relatively straight forward. A strong northwest-southeast structural alignment occurs across the Fork, Coldwater and Sherman townships. It is along the axis of this fold that the three major producing oil fields of the area are located. The Fork oil field (Fork township) and the

Coldwater oil field (Coldwater township), situated on the major fold, both have a minor axis in a northeast-southwest direction which may line-up with, or tend to parallel, the structural high occurring in the northern half of Martiny township (T.15 N., R.8 W.). The Sherman oil field (Sherman township) also lies on the axis of the major northwest-southeast fold.

Another northwest-southeast fold of a smaller magnitude cuts across the northeastern portion of Nottawa township. A small closure on this fold results in the Beal City oil field. A small portion of a third northwest-southeast fold cuts across the northeast corner of the area studied (T.16 N., R.4 W.).

A deep synclinal trough lies in the northeastern portion of Gilmore township and trends parallel with the major structural alignment of the area studied.

The regional dip of the entire area is to the northeast with major folding in a northwest-southeast direction and a cross-folding of minor importance in a northeast-southwest direction. Four major oil fields exist in the area with several minor and one-well fields.

Lithologic Ratio Maps

The ratio of magnesium to calcium provided data for a lithologic ratio map showing the relative degree of dolomitization at the locations of samples analyzed. The values of the ratios for the top five feet of the Rogers

City formation were first plotted and lines of equal ratio values were drawn providing a geometric contour interval. (Map 3--See pocket.)

An average of the Mg/Ca ratio values was then determined for each well analyzed and plotted to show the degree and pattern of dolomitization for the top 20 feet of the Rogers City limestone. (Map 4--See pocket.)

Interpretation of Lithologic Ratio Maps

The lithologic Mg/Ca ratio maps show the areal variation in the degree of secondary dolomitization over the area studied. Comparing Map 3 with Map 4 a vertical variability can be observed.

The degree of dolomitization appears, in general, to increase on the apices of the major folds. There is a definite relation, in general, between the degree of dolomitization and the magnitude of the structure. The structural trend and the trend existing in the contouring of the ratio values show a close correlation in general.

There is an exception to this observation in the southeast portion of Chippewa township and the southwest portion of Fork township. Here is an area with a high degree of dolomitization lying in a structural "low" with no production of oil. There are a number of reasons which may be proposed to explain this situation: (1) fracturing and faulting, or original porosity, may have led to secondary dolomitization in the trough area, or (2)

dolomite-formation may have been complete leaving no porosity for the accumulation of oil; or (3) there was porosity in the secondary dolomite but unfavorable conditions for the accumulation of oil.

The degree of dolomitization which appears, in general, to be related to the minor cross-folding shows a stronger trend than does the actual structural alignment. This may be due either to fracturing and fissuring along the axis of the minor folds, or to an original porosity in the limestone formed along the apices of the folds leading to later dolomitization. (Compare Map 2 with Maps 3 and 4.)

Comparing Maps 3 and 4, there would appear to be no significant difference in the vertical variation of dolomitization between the upper five feet of the limestone formation and a total over-all average of the top twenty feet, thus, giving no evidence, one way or the other, as to ascending or descending mineralizing waters; assuming there were such waters.

Coldwater Oil Field

A more detailed study was made of the Coldwater oil field with a chemical analysis of twenty-five samples selected from the producing structure. This close-up study was made to compare the degree and pattern of dolomitization locally as related to a well defined and prolific structure.

Structure contour map.--A structure contour map was plotted and interpolated on the available data for the Coldwater oil field. (See Map 5.) The regional dip of the field is to the northeast and the steepest dips of the Coldwater structure are found along the northeast side of the field.

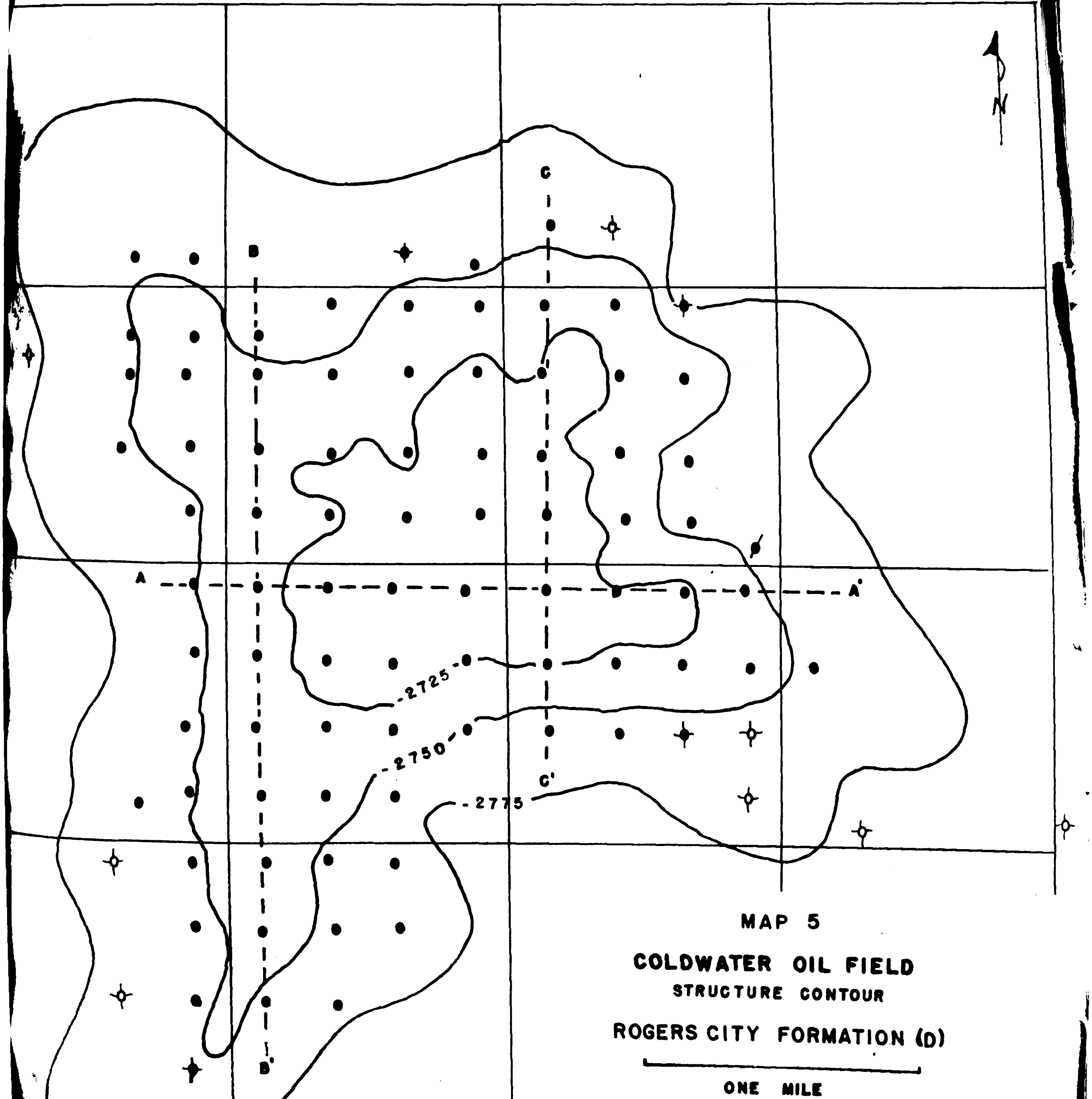
The major axis of the field has a northwest-southeast alignment and a minor axis trending northeast-southwest. The Coldwater structure has a closure of 40 to 50 feet on the Rogers City formation.

Lithologic ratio map.--The average Mg/Ca ratios for approximately the top 10 feet of the Rogers City limestone were plotted for each of the 25 wells in the field to show the relative degree of dolomitization and its possible relationship to that of the Coldwater structure. (See Map 6.)

Interpretation of lithologic ratio map.--The lithologic Mg/Ca ratio map shows the areal variation in the degree of secondary dolomitization within the top 10 feet of the Rogers City limestone of the Coldwater structure.

The pattern of dolomitization coincides closely with the structure alignment of the field. The degree of dolomitization increases on the apices of the major and minor folds, with a more pronounced trend appearing along the minor axis than that evident on the structure contour map.

An exception to the coincidence of structure and degree of dolomitization is the re-entrant angle in the



MAP 5

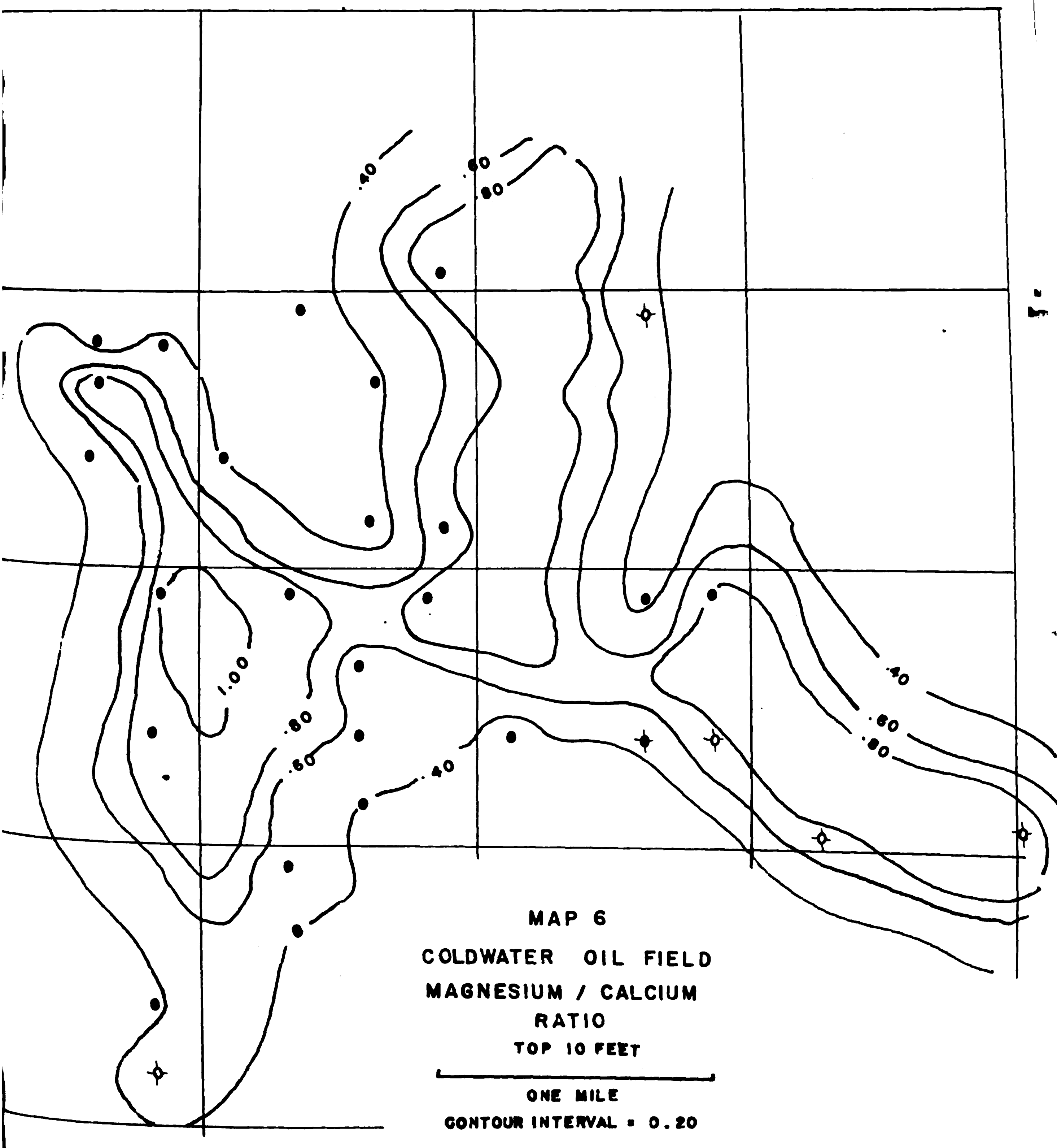
COLDWATER OIL FIELD

STRUCTURE CONTOUR

ROGERS CITY FORMATION (D)

ONE MILE

CONTOUR INTERVAL = 25 FEET



MAP 6
COLDWATER OIL FIELD
MAGNESIUM / CALCIUM
RATIO
TOP 10 FEET

ONE MILE
CONTOUR INTERVAL = 0.20

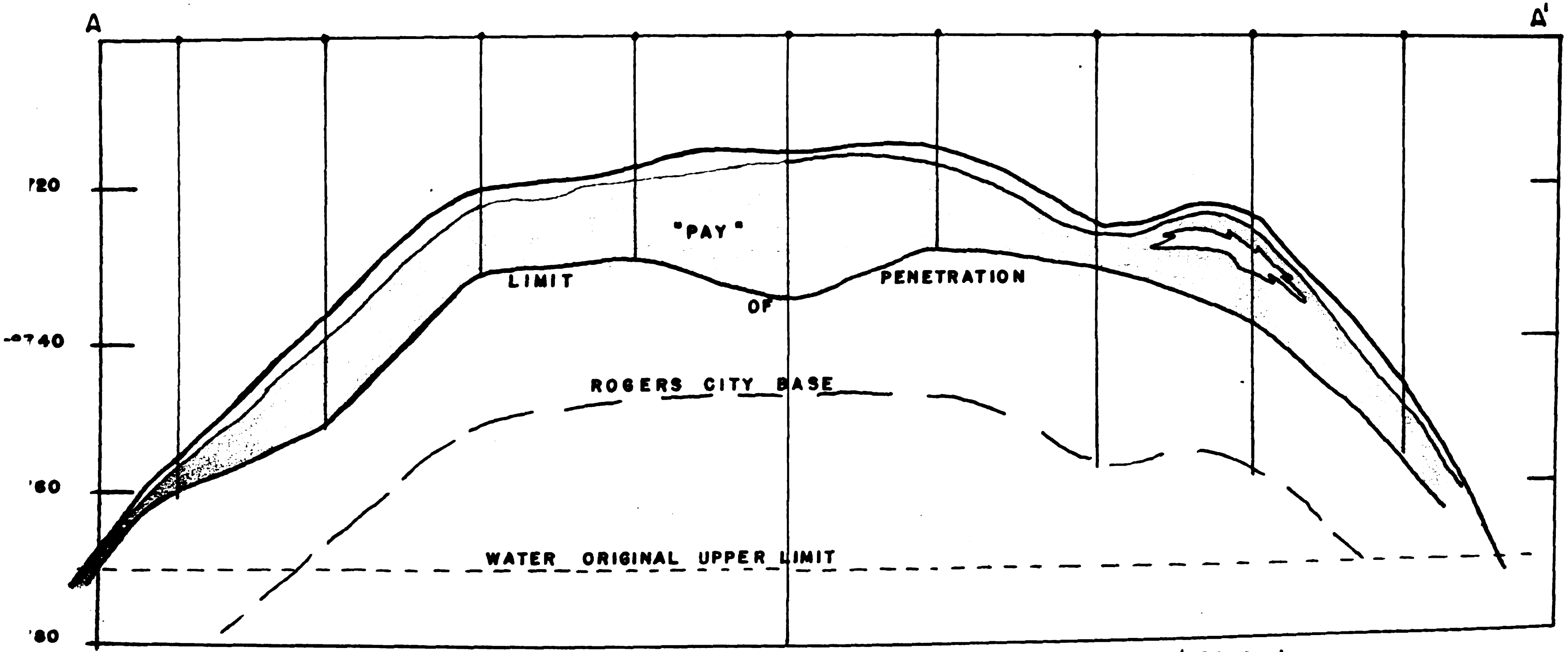
pattern of dolomitization on the north side of the field. This area of reduced secondary dolomitization of the Rogers City limestone lies parallel to the major axis of the structure and may be due to a decrease in fissures or tension cracks on the lower flank of the major axial fold.

Vertical configuration and pay zones.--Cross sections were drawn to a scale of 4 inches per mile horizontally and 1 inch per 20 feet vertically, to show the configuration of the top of the Rogers City formation and the position of the reservoir within it. The pays are shaded in the drawings and represent actual reservoir space as determined from the drilling records of producing wells and dry holes (Knapp, 1950).

Cross section A-A' (Figure 2) shows the east-west configuration and pay zones across sections 31, 32, and 33 (Coldwater township). Cross sections B-B' (Figure 3) and C-C' (Figure 4) give the north-south configuration of the field through sections 29, 32, (Coldwater township) and 5 (Sherman township) and sections 21 and 33 (Coldwater township), respectively.

Core analysis records show that lateral permeability exceeds the vertical permeability due to horizontally bedded dense and porous zones in the Rogers City formation. The configuration and pay zone pattern, as observed in the above cross sections, make it quite "evident that the Coldwater reservoir is not an open, freely-connected system

Figure 2. East-west cross-section of the Coldwater Oil Field showing configuration of structure and pay zones in the Rogers City formation. See Map 5 for location of cross-section A-A'. (After T.S. Knapp, 1950?)



Horizontal Scale 4 inches / 1 mile Vertical Scale 1 inch / 20 feet configuration of

Figure 3. North-south cross-section of the Coldwater Oil Field showing configuration of structure and pay zones in the Rogers City formation. See Map 5 for location of cross-section B-B'. (After T.S. Knapp, 1950?)

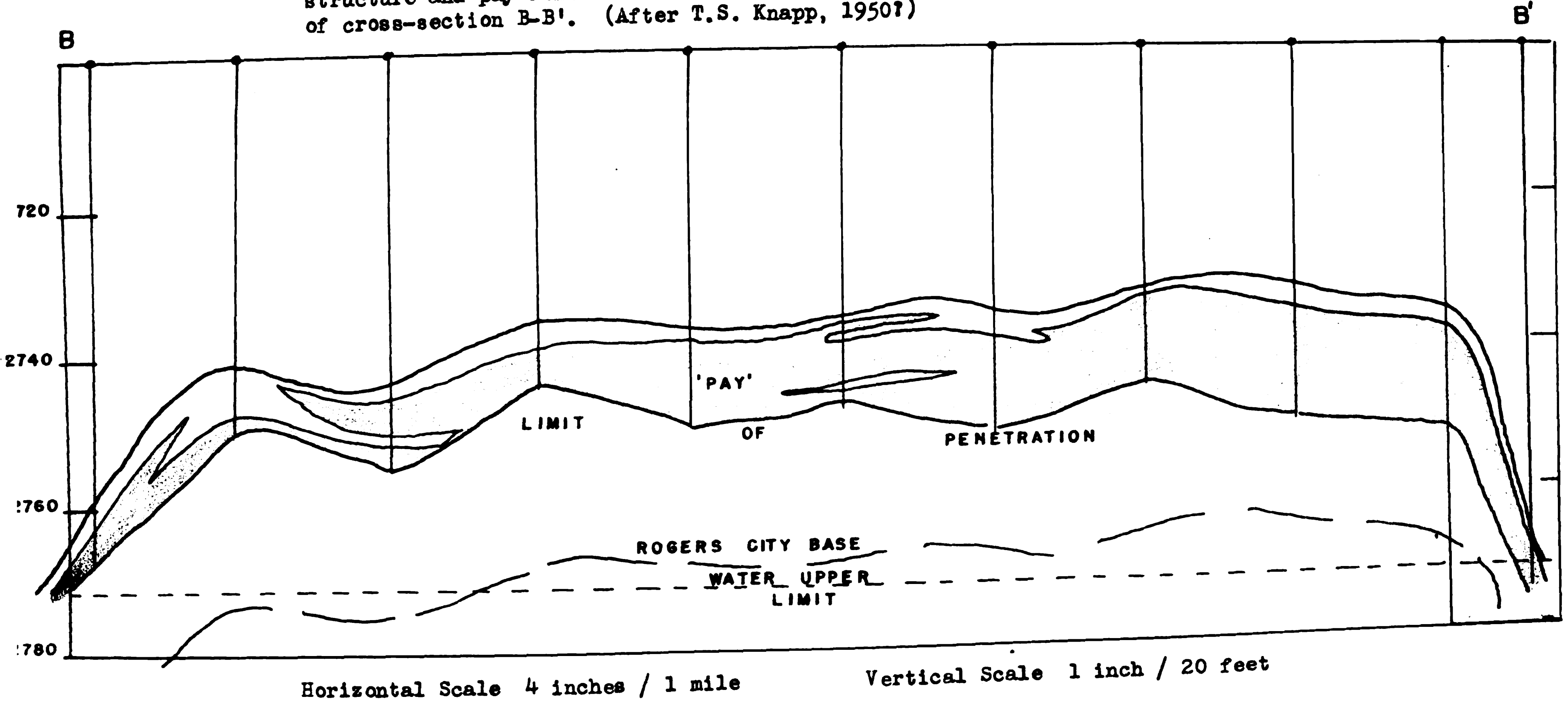
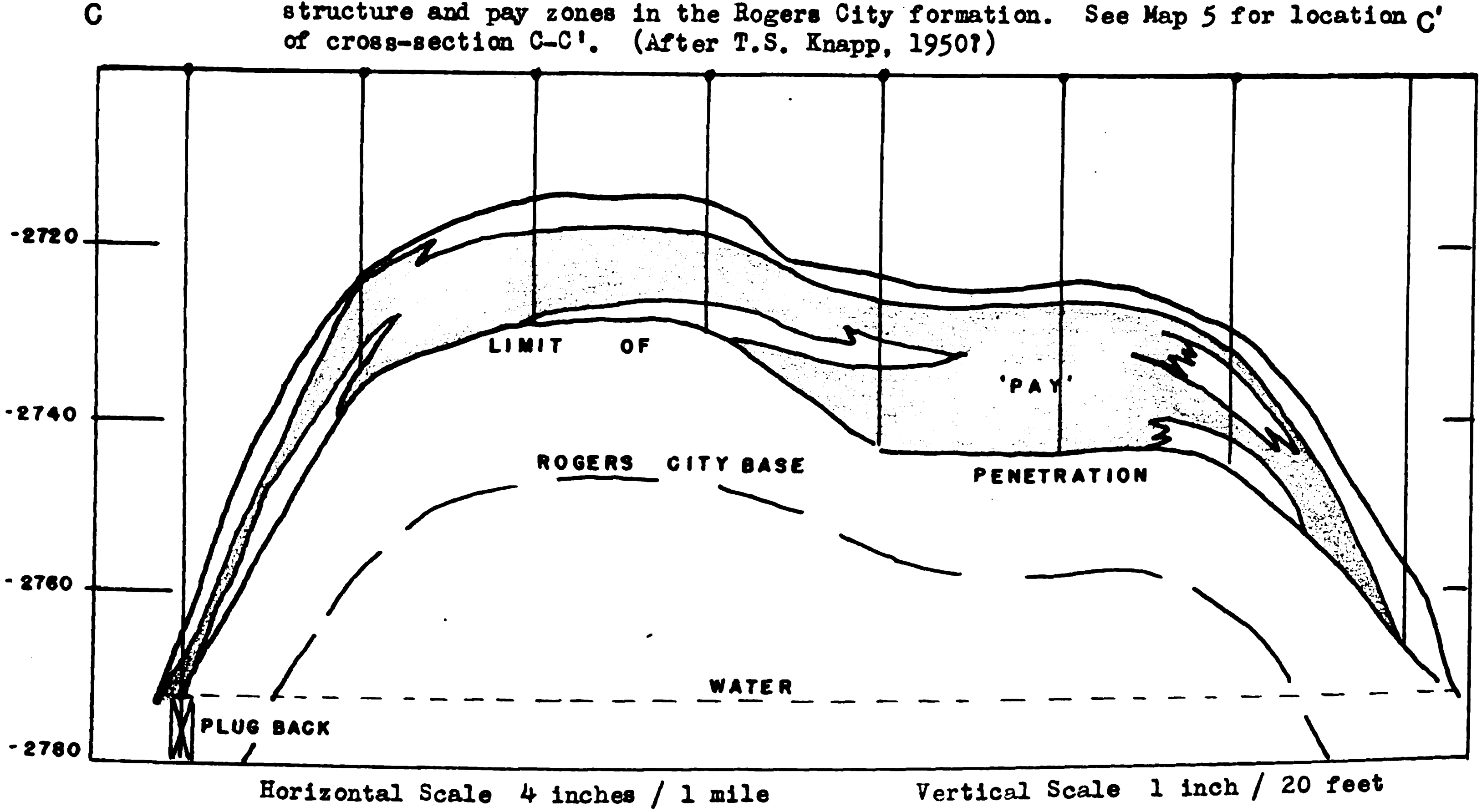


Figure 4. North-south cross-section of the Coldwater Oil Field showing configuration of structure and pay zones in the Rogers City formation. See Map 5 for location of cross-section C-C'. (After T.S. Knapp, 1950?)



of spaces" (Knapp, 1950). The lenticular-like chambers are governed to a certain extent by bedding, whereas, many of the porous zones (secondary dolomitized limestone) are due to a haphazard arrangement of vertical fractures consisting of large, open and continuous fissures and small, short and completely filled ones (Knapp, 1950).

A combined study of the cross sections of the top 10 feet of the Rogers City formation and the lithologic Mg/Ca ratio map of the Coldwater field gives a fair picture of the reservoir system and pay zone configuration of the Coldwater oil field.

Statistical Interpretation

Statistical Methods

The statistical interpretations made in this study of the laboratory results were based upon the methods of "analysis of variance." "Basically the analysis of variance is a simple arithmetical method of sorting out the components of variation in a given set of results" (Goulden, 1952). The complete analysis of variance actually performs a dual role. First, there is the sorting out and estimation of the variance components,[1] and secondly, it provides for tests of significance.

---

[1] The term "component" is used here with reference to the integral parts, or component parts of the variation within the set of results.

A detailed description of the method and calculations for an analysis of variance is not given here but can be found in most statistics texts (Goulden, 1952; Dixon and Massey, 1951). The "F" ratio was used for the tests of significance in the analysis of variance; principles and computations of which are given in all statistics textbooks (Goulden, 1952; Dixon and Massey, 1951).

Statistical Interpretation of Data

I. Producing "high" versus non-producing "low".--Using the Mg/Ca ratios from nineteen producing wells selected on "high" structures as compared to the Mg/Ca ratios of nineteen non-producing wells selected on "low" structures, a combined analysis of variance was made pertaining to the variance components: (1) between wells, (2) between producing or non-producing structures, (3) between levels of 0 to 5 feet and 5 to 10 feet from the top of the Rogers City formation, and (4) the interactions between structures times levels and levels times wells. (See Table 2.)

See Figure 5 for the complete analysis of variance of the above situation.

Conclusion.--There is a highly significant difference (beyond the 1% level) between the averages of the Mg/Ca ratios of the thirty-eight wells considered. Although statistically significant there would appear to be no important significance geologically as uniform dolomitization of the limestone would not be expected.

TABLE 2

DATA FOR AN ANALYSIS OF VARIANCE

Producing "High" Versus Non-Producing "Low"
Magnesium/Calcium Ratios

Producing "High"	Well Numbers		Non-Producing "Low"
0.328[a]	11	2	0.578
0.377[b]			0.436
0.561	16	19	0.090
0.451			0.087
0.833	56	21	1.443
0.689			0.835
0.813	67	23	0.669
0.991			0.387
1.399	68	26	0.433
0.707			0.387
0.320	74	28	0.712
0.368			0.607
0.366	75	34	0.408
0.401			0.232
0.395	76	36	0.153
0.482			0.275
0.329	82	37	0.183
0.910			0.142
0.837	83	41	0.265
0.870			0.438
0.484	84	42	0.208
1.356			0.122
0.955	85	49	0.123
0.871			0.114
0.888	86	50	0.151
0.981			0.150
1.067	87	51	0.913
0.909			0.617
0.444	90	53	0.500
0.357			0.445
0.273	91	54	0.384
0.455			0.270
0.510	92	58	0.380
0.409			0.948
1.276	93	64	0.508
0.458			0.283
0.328	95	69	0.542
0.559			0.505
12.406[a]	Total		8.643[a]
12.601[b]	Total		7.280[b]
0.658	Average		0.419

[a] 0 to 5 foot interval

[b] 5 to 10 foot interval

PRODUCING "HIGH" VERSUS NON-PRODUCING "LOW"

Source of Variance	D.F.[1]	Sums of Squares	Mean Square	F
Total	75	7.771		
Wells	36	4.924	0.1368	2.880**
Types[2]	1	1.089	1.089	22.930**
Levels[3]	1	0.021	0.021	0.442
Types x Levels	1	0.028	0.028	0.589
Levels x Wells	36	1.709	0.047	

Figure 5. Analysis of variance

[1] Degrees of freedom
[2] Producing "High" and Non-Producing "Low" Structures
[3] Depth of 0-5 feet and 5-10 feet
**Highly significant beyond the 1% level

The highly significant difference (beyond the 1% level) between the averages of the Mg/Ca ratios of the producing "high" structures and non-producing "low" structures would tend to show, statistically, a relationship between increasing dolomitization and producing wells on "high" structures. The mean of the Mg/Ca ratios for the producing "high" was 0.658 and for the non-producing "low" 0.419.

There was no statistical difference between the averages of the Mg/Ca ratios of the upper 0 to 5 feet of the formation as compared to those of the lower 5 to 10 feet.

There was no significant interactions between types times levels or between levels times wells. This would imply that "there is no difference in the means of the subgroups after the cell means have been 'adjusted' for" well, type and level effects (Dixon and Massey, 1951, p. 138).

II. Producing "high" versus non-producing "high."-- Using the Mg/Ca ratios from ten producing wells randomly selected on "high" structures as compared to the Mg/Ca ratios of ten non-producing wells selected on "high" structures, a combined analysis of variance was made pertaining to the variance components: (1) between wells, (2) between producing and non-producing wells both on "high" structures, (3) between levels of 0 to 5 feet and 5 to 10 feet from the top of the Rogers City formation, and (4) the interactions between types times levels and levels times wells. (See Table 3.)

See Figure 6 for the complete analysis of variance of the above situation.

Conclusion.-- Statistically there is no significant difference between the averages of the Mg/Ca ratios of the wells located on "high" structures. This would appear to indicate that the degree of dolomitization along the "high" structures is more uniform than between "high" and "low" structures. There is no significant difference between the averages of the Mg/Ca ratios of producing and non-producing wells all located on "high" structures. The mean of the Mg/Ca ratios for the producing wells is 0.590 and for those of the non-producing wells is 0.558. The relationship as

TABLE 3

DATA FOR ANALYSIS OF VARIANCE

A. Producing "High" Versus Non-Producing "High"
B. Non-Producing "High" Versus Non-Producing "Low"

Magnesium/Calcium Ratios

Producing "High" (Random)		Non-Producing "High"		Non-Producing "Low" (Random)	
Well No.	$\frac{Mg}{Ca}$	Well No.	$\frac{Mg}{Ca}$	Well No.	$\frac{Mg}{Ca}$
76	0.395[a]	27	0.359[a]	53	0.500[a]
	0.482[b]		0.370[b]		0.446[b]
56	0.833	29	0.511	54	0.384
	0.689		0.180		0.270
91	0.273	38	1.058	37	0.183
	0.455		0.355		0.142
68	1.399	39	0.887	36	0.153
	0.707		0.271		0.275
82	0.329	45	0.745	51	0.913
	0.910		0.488		0.617
75	0.366	47	0.364	64	0.508
	0.401		0.104		0.283
86	0.888	62	0.668	23	0.669
	0.981		1.381		0.387
90	0.444	63	1.039	42	0.208
	0.357		0.467		0.122
16	0.561	65	0.699	41	0.265
	0.451		0.426		0.438
95	0.328	70	0.385	69	0.542
	0.559		0.405		0.505
Total[a]	5.816		6.715		4.325
Total[b]	5.992		4.448		3.484
Average	0.590		0.558		0.390

[a] 0 to 5 foot interval

[b] 5 to 10 foot interval

PRODUCING "HIGH" VERSUS NON-PRODUCING "HIGH"

Source of Variance	D.F.	Sums of Squares	Mean Square	F
Total	39	3.584		
Wells	18	2.081	0.1156	1.685
Levels	1	0.109	0.1090	1.589
Types[1]	1	0.010	0.0100	0.146
Types x Levels	1	0.150	0.1500	2.187
Levels x Wells	18	1.234	0.0686	

Figure 6. Analysis of variance

[1] Producing "High" and Non-Producing "High" structures

determined statistically between the possibility of a producing well or a non-producing well depends on factors other than the degree of dolomitization and structure alone. A high degree of dolomitization on a favorable structure, although a good indication, geologically, of a producing well, is not an exclusive confirmation.

There was no significant interaction between types and levels or levels and wells.

III. Non-producing "high" versus non-producing "low."--Using the Mg/Ca ratios from ten non-producing wells selected on "high" structures as compared to the Mg/Ca ratios of ten non-producing wells randomly selected from "low" structures, a combined analysis of variance was made pertaining to the variance components: (1) between wells, (2) between non-producing "high" and "low" structures,

(3) between levels of 0 to 5 feet and 5 to 10 feet from the top of the Rogers City formation, and (4) the interactions between types times levels and levels times wells. (See Table 3.)

See Figure 7 for the complete analysis of variance of the above situation.

NON-PRODUCING "HIGH" VERSUS NON-PRODUCING "LOW"

Source of Variance	D.F.	Sums of Squares	Mean Square	F
Total	39	3.078		
Wells	18	1.639	0.0911	1.894
Levels	1	0.242	0.2420	5.031*
Types[1]	1	0.282	0.2820	5.863*
Types x Levels	1	0.050	0.0500	1.040
Levels x Wells	18	0.865	0.0481	

Figure 7. Analysis of variance

[1] Non-Producing "High" and Non-Producing "Low" structures
*Significantly different at the 5% level

Conclusion.--Statistically there is a significant difference (at the 5% level) between the averages of the Mg/Ca ratios of the upper 0 to 5 feet and the 5 to 10 foot depths. The means of the Mg/Ca ratios for non-producing wells on "high" structures at 0 to 5 feet and 5 to 10 feet are 0.67 and 0.44, respectively; the means of the Mg/Ca ratios for non-producing wells on "low" structures at 0 to 5 feet and 5 to 10 feet are 0.43 and 0.34, respectively.

This comparison, as based upon 20 non-producing wells, would not appear to be of any geological significance.

The significant differences (at the 5% level) between the averages of the Mg/Ca ratios for the non-producing "high" and non-producing "low" structures would tend to support the belief of a direct relationship of "high" structure to increasing degree of dolomitization. The mean of the Mg/Ca ratios for the "high" structure is 0.558 and for the "low" structure is 0.39.

There is no significant interaction between types times levels or between levels times wells.

IV. "High" versus "low" structure.--Using the Mg/Ca ratios from nineteen wells selected randomly from "high" structures as compared to the Mg/Ca ratios of nineteen wells randomly selected from "low" structures, a combined analysis of variance was made pertaining to the variance components: (1) between wells, (2) between "high" and "low" structures regardless of production or non-production, (3) between levels of 0 to 7.5 feet and 7.5 to 15 feet from the top of the Rogers City formation, and (4) the interactions between types times levels and levels times wells. (See Table 4.)

See Figure 8 for the complete analysis of variance of the above situation.

TABLE 4

DATA FOR AN ANALYSIS OF VARIANCE

"High" Versus "Low"--Magnesium/Calcium Ratios

"High"	Well Numbers		"Low"
1.939[a]	5	2	0.578
1.278[b]			0.436
0.328	11	6	1.439
0.377			1.303
0.346	29	12	0.335
0.305			0.421
0.707	38	14	0.720
0.731			0.624
0.887	39	18	0.152
0.271			0.250
0.578	45	19	0.085
0.448			0.287
0.234	47	25	0.180
0.171			0.281
1.009	60	28	0.660
0.819			0.579
0.368	61	30	0.501
0.200			0.720
0.668	62	35	0.486
1.381			0.375
0.813	67	40	0.119
0.991			0.105
0.385	70	41	0.357
0.405			0.236
0.395	76	43	0.159
0.472			0.185
0.293	77	48	0.354
0.312			0.131
0.874	83	50	0.150
1.027			0.289
0.888	86	58	0.380
0.981			0.948
0.401	90	57	0.792
0.365			0.850
0.510	92	69	0.542
0.409			0.505
1.276	93	80	0.139
0.427			0.184
12.899[a]	Total		8.128
11.370[b]	Total		8.709
0.639	Average		0.443

[a] 0 to 7.5 foot interval [b] 7.5 to 15 foot interval

"HIGH" VERSUS "LOW"

Source of Variance	D.F.	Sums of Squares	Mean Square	F
Total	75	10.177		
Wells	36	8.045	0.2235	6.024**
Types[1]	1	0.727	0.7270	19.596**
Levels	1	0.012	0.0120	0.323
Types x Levels	1	0.058	0.0580	1.563
Levels x Wells	36	1.335	0.0371	

Figure 8. Analysis of variance

[1] "High" and "Low" structures
**Highly significant beyond the 1% level

Conclusion.--The difference between the averages of the Mg/Ca ratios of the 38 wells is highly significant (beyond the 1% level). This would have no significance geologically as uniform dolomitization would not be expected over this area.

The highly significant difference (beyond the 1% level) between the averages of the Mg/Ca ratios, or degree of dolomitization, between the well samples from "high" structures and those of "low" structures is of geologic importance. It would appear, from statistical evidence, that there is a direct relationship between the magnitude of structure and the degree of dolomitization. In general, the greater the relief of structure the greater the degree of dolomitization. The mean of Mg/Ca ratios for the "high" was 0.639 and for the "low" was 0.443. (See Table 4.)

There was no significant interaction between types times levels or between levels times wells.

V. Producing "high" versus non-producing "low" in iron content.--Using the percentage iron content from nineteen producing wells selected on "high" structures as compared to the percentage iron content of nineteen non-producing wells selected on "low" structures, a combined analysis of variance was made pertaining to the variance components: (1) between wells, (2) between producing and non-producing structures, (3) between levels of 0 to 5 feet and 5 to 10 feet from the top of the Rogers City formation, and (4) the interactions between types times levels and levels times wells. (See Table 5.)

See Figure 9 for the complete analysis of variance of the above situation.

Conclusion.--There is a highly significant difference (beyond the 1% level) of the average iron content between the wells, between the 0 to 5 and 5 to 10 foot intervals or levels, and between the producing "high" and the non-producing "low" structures. The iron content is higher in the non-producing "low" structures with a mean of 1.62% as compared to 1.18 % in the producing "high" structures. The 0 to 5 foot interval from the top of the formation is consistently higher in iron than the next five foot interval. The mean iron content of the top 5 feet

TABLE 5

DATA FOR AN ANALYSIS OF VARIANCE

Producing "High" Versus Non-Producing "Low" Percentage Iron Content

Producing "High"	Well Numbers		Non-Producing "Low"
0.90[a]	11	2	1.34
0.58[b]			0.70
1.18	16	19	2.60
1.14			2.37
0.95	56	21	4.16
0.68			2.86
0.80	67	23	3.28
0.73			2.30
1.69	68	26	0.50
1.13			0.46
1.60	74	28	2.00
0.80			1.32
0.60	75	34	2.24
0.56			1.60
0.64	76	36	1.90
0.56			1.00
1.44	82	37	2.06
1.50			0.98
1.64	83	41	2.44
0.98			1.15
2.98	84	42	1.24
3.20			1.04
1.34	85	49	0.76
1.54			0.75
1.32	86	50	0.70
0.64			0.92
1.44	87	51	0.70
0.80			0.56
0.90	90	53	1.14
0.98			1.04
1.78	91	54	0.94
0.74			0.82
1.44	92	58	4.04
0.88			3.24
2.44	93	64	2.96
0.76			1.04
0.74	95	69	1.50
0.74			0.98
25.82[a]	Total		36.50
18.94[b]	Total		25.12
1.18	Average		1.62

[a] 0 to 5 foot interval

[b] 5 to 10 foot interval

for the "high" and "low" structures is 1.64% while that of the next five foot interval for the combined "high" and "low" structures is 1.16%.

PRODUCING "HIGH" VERSUS NON-PRODUCING "LOW"
IRON CONTENT

Source of Variance	D.F.	Sums of Squares	Mean Square	F
Total	75	55.10		
Wells	36	41.76	1.160	8.529**
Types[1]	1	3.79	3.79	27.87 **
Levels	1	4.44	4.44	32.65 **
Types x Levels	1	0.22	0.22	1.60
Levels x Wells	36	4.89	0.136	

Figure 9. Analysis of variance

[1] Producing "High" and Non-Producing "Low" structures
**Highly significant beyond the 1% level

There is no significant interaction between types times levels or between levels times wells.

There would appear to be a decrease in the content of iron with an increase in the degree of dolomitization in the light of the statistical results.

ORIGIN OF DOLOMITE IN THE ROGERS CITY LIMESTONE

A number of possibilities exist as to the origin of the dolomite within the top twenty feet of the Rogers City Limestone.

The contention of some geologists that an unconformity exists at the top of the Rogers City formation and the base of the Bell shale, if true, could possibly be the basis for an explanation of the dolomitized limestone. R. B. Newcombe (1930) in his studies in western Michigan proposed that an unconformity exists because of the erosion of the Dundee beds and because of the non-deposition of the lower part of the Traverse group and the Bell shale. "This Middle Devonian unconformity at the base of the Traverse group," he explained, "amounts to a westward progressive overlap by which the Bell and Dundee are unrepresented in the southwestern part of Michigan." One kind of evidence Newcombe (1930) offered to support the contention for this unconformity was that "the existence of an erosion surface is shown by dolomitization, character of porosity, and features of a pre-Traverse topography." This erosion surface, he stated, "was due to a sudden drop in sea level which revived the streams, made the sea more muddy, and led to extensive erosion of the mantle of Dundee and Monroe beds" (Newcombe, 1930).

Ehlers and Radabaugh (1938) supported this theory with their study of the Dundee in Presque Isle County, Michigan. There, they stated: "The contact of the Rogers City limestone with the overlying Bell shale is disconformable; the effects of erosion of the Rogers City limestone prior to the deposition of the Bell shale are well illustrated by solution channels, crevices and small caverns all subsequently filled with the Bell shale" (Ehlers and Radabaugh, 1938).

K. K. Landes (1951) stated that "emergence followed the deposition of Dundee and Rogers City strata and subsequent erosion stripped these rocks from the southwestern corner of Michigan and again exposed the Detroit River group at the surface."

If the top of the Dundee were exposed throughout the entire southern peninsula of Michigan, then the formation of an erosion surface could result in the highly porous zone (Rogers City formation) beneath the contact of the younger Bell shale. The solution channels and cavities within the limestone would allow easy passage to ascending waters at the time of dolomitization, possibly at the time of, or after, the period of folding late in the history of the Michigan basin.

If the central portion of the Michigan basin was not entirely exposed the Rogers City formation may be the result of an eroded and redeposited limestone as a clastic sediment which in turn may have resulted in a more porous rock that was easily dolomitized later during folding of the beds in the basin.

The theory of leaching might be applied as an alternative to that of the replacement theory in this instance. "Both calcium carbonate ($CaCO_3$) and ferrous hydrocarbonate ($Fe(HCO_3)$) are more soluble in ground waters, commonly a carbonic acid solution, than the magnesium carbonate ($MgCO_3$); thus, they are subject to leaching" (Mellor, 1932). The removal of the calcium and ferrous carbonates gives rise to a concentration of the magnesium carbonate. It has been the view of many geologists that dolomites might have resulted from surface or marine leaching in this manner.

The theory of leaching might explain the possibility of a more rapid removal of the calcium and iron from the fractured and fissured anticlines and little or no leaching in the troughs or synclines, but it would not explain the consistent decrease in the iron content from the top of the formation downward regardless of structure.

Core analyses and well samples show no apparent break between the Rogers City formation and the contact of the overlying Bell shale (Knapp, 1950). If this be the case, and in the light of the present study, it would appear that with the folding of the sedimentary beds minor fractures and fissures were developed throughout the central basin. Secondary dolomitization of the limestone formation probably took place in areas of circulating ground waters, possibly ascending at the time of dolomitization from lower depths through older, regional dolomites (Detroit River and Dundee) and carrying magnesium from those rocks. The possibility as to why the dolomitization is confined largely to the upper part of the limestones may be due to the presence of the overlying Bell shale which might partially block the ascending solutions so that they spread out and moved laterally in the upper part of the limestone. The upper-most portions of the limestones would be the apices of the anticlinal folds and may explain the relationship of structure to degree of dolomitization. Also, more tensional cracks and fissures would tend to form on the folded anticlines than in the synclinal troughs.

The iron content of the limestone formation exists in the form of a carbonate. "The carbonates of iron and manganese--frequently enter replacing the magnesium carbonate (of dolomite) and grade to ankerite" (Dana, 1951). A replacement of one-third of the Mg atoms by Fe does not change the character of the dolomite crystalline structure. Normal dolomite ($CaCO_3 \cdot MgCO_3$) may readily grade into ankerite ($2CaCo_3.MgCO_3.FeCO_3$). Minerals that may be classed as ankerite have in general the same mode of occurrence and associations as dolomite. As the indices of dolomite ($o = 1.68$ and $e = 1.50$) increase with an increase of iron or manganese it is difficult to distinguish it optically from ankerite (o = 1.72 and e = 1.53) (Dana, 1951).

It would appear, from all available evidence, that the magnesium replaced the calcium by solutions ascending by means of the fractures and fissures concentrated in the anticlinal structures. On the other hand, the ferruginous waters descending from overlying formations rich in iron may have concentrated in the trough-like depressions and replaced the Mg atoms with Fe atoms giving rise to a ferrous dolomite or possibly an ankerite.

It should be noted, in closing, that the samples analyzed vary in iron content from 0.46% to 4.16%. This variation of less than 4.00% may be so insignificant as to warrant little attention in consideration of the theory of the origin of the Rogers City dolomite.

SUMMARY AND CONCLUSION

General Summary

The rapid and accurate methods described in this paper for the determination of calcium and magnesium content of carbonate rocks make it possible to run routine analyses of a large number of samples. The methods used were adopted by the author from Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, published by the American Public Health Association, 1955, for the determination of the calcium, magnesium, and iron content in water hardness tests. The error encountered in the chemical analyses ranged from plus or minus .005% for the calcium test to plus or minus 1% for the magnesium and iron tests.

The above-mentioned techniques were used to analyze dolomitic limestones from the Rogers City formation of the central Michigan basin area. The Rogers City-Dundee formation, normally a marine limestone, is found in many places to be an extremely porous dolomite. Production is generally limited to these dolomitic zones in fields producing oil from the Rogers City formation. It is the nature and origin of these dolomitic zones which were the concern of this paper.

The preparation of lithologic Mg/Ca ratio maps is an ideal means to depict the lateral variation in the degree of dolomitization over the area studied. A comparison of structural maps and Mg/Ca ratio maps make it possible to observe actual relationships between structure and degree of dolomitization; whereas, comparison of Mg/Ca ratio maps determined for different depths of the Rogers City formation allows one to note vertical variation in the pattern of secondary dolomitization.

The simultaneous correlations and comparisons of several variables both laterally and vertically, which could not be diagramed readily in three dimension, were compared by the statistical method of the analysis of variance. Statistically, combinations of variables can be analyzed for possible relationships that would be impossible or impracticable to produce on maps.

Conclusions

The comparison of structural and ratio maps of the Rogers City limestone and the Coldwater oil field reveals, in general, a significant relationship between the structure and the degree of dolomitization as indicated by the Mg/Ca ratio. There would appear to be a direct relationship both regionally and locally between "high" structure and an increase in the degree of dolomitization.

One exception to this relationship was observed in the comparison of the structural and ratio maps. An area of locally dolomitized limestone did not coincide with a structural "high" but was located in a structural trough or "low." Unfortunately, then, the discovery of a body of locally dolomitized limestone does not insure finding gas or oil. It has been found elsewhere that local dolomites are non-porous, or that they are so situated structurally that no suitable trap for oil accumulation exists and therefore are non-productive. These facts were recognized by Orton (1888), who pointed out nearly seventy years ago, that in the Trenton dolomite fields of Ohio and Indiana a combination of porosity and favorable structural position was necessary for commercial oil and gas accumulation. Lacking any further evidence, it would seem that unfavorable structure may be the cause of non-production in this area of locally dolomitized limestone.

Upon comparison of the Mg/Ca ratio maps for the top five feet of the Rogers City limestone with the average ratios of the top twenty feet there would appear to be no significant relationship or pattern of dolomitization with changing depths. The same conclusion was arrived at statistically, showing no significant difference in the pattern or variation of dolomitization between the top five feet and the next five feet, or between the top 7.5 feet and the next 7.5 feet.

In this respect, there is no evidence for, or against, the possibility of ascending or descending solutions which may have caused the dolomitization of the limestone.

The results of the statistical comparisons were as follows:

1. There is a highly significant difference between the Mg/Ca ratios of the producing wells on "high" structures, as compared to those of the non-producing wells on "low" structures. Expressing a "producing" well in terms of "porosity," there is a relationship between porosity and degree of dolomitization.
2. There is no significant difference between the Mg/Ca ratios of producing wells and non-producing wells all on "high" structures. The degree of dolomitization is high for both producing and non-producing wells. Therefore, there is either little or no porosity in the replacing dolomite or other factors are responsible for the non-productive nature of the wells.
3. There is a significant difference between the Mg/Ca ratios of non-producing wells on "high" structures as compared to those on"low" structures. The degree of dolomitization is much smaller in troughs, or "low" structures, as compared to the structures of greater magnitude.
4. There is a highly significant difference between the Mg/Ca ratios of "high" structures as compared to those of "low" structures regardless of producing or non-producing wells.

There would appear to be a direct relationship, in general, between magnitude of structure and degree of dolomitization. Although there is a relationship between degree of dolomitization and porosity it is no simple and direct relationship which would exist in an ideal case when all porosity is caused by dolomitization. The lack of perfect correlation is probably due to the existence of some pores or fractures prior to dolomitization.

5. There is a highly significant difference in the iron content between the producing wells on "high" structures and the non-producing wells on "low" structures. The iron content is consistently greater on "low" structure with a minimum of secondary dolomitization.
6. There is a highly significant difference between the iron content of the top five foot interval as compared to the next five foot interval of the Rogers City formation. The top five feet of the formation contains a greater per cent of iron than does the next five foot interval regardless of structural relief.

On the basis of the thirty-eight wells analyzed statistically on percentage of iron content it would appear that the ferrous solutions were descending from overlying formations with a tendency to concentrate in the troughs or synclinal structures replacing the Mg atom with an Fe atom in the dolomite crystalline structure. The resulting secondary replacement is a ferrous dolomite with the eventual possibility of grading into the mineral ankerite. The concept of descending ferrous solutions would explain the decrease in per cent iron content from the top of the Rogers City formation downward. However, the variation of less than 4.00% in the iron content of the samples analyzed statistically may be insignificant for a regional consideration and thus warrant little or no attention.

The magnesium to calcium ratio in limestones is a very useful geologic tool. It is especially useful in porosity studies of dolomitized limestone formations. The rapid and accurate techniques used in this study can enable geologists and petroleum engineers to make the Mg/Ca ratio determination a routine analysis. Statistical studies may enable them to predict porosity of carbonate rocks. Statistical studies may also show the relationship between porosity and dolomitization for many limestones, which have been reported as lacking such relationship (Chilingar and Terry, 1954).

Ratio determinations may also be useful in locating dolomitized structures or trends of structural highs in areas of little structural control. The Mg/Ca ratios should aid in locating and following dolomitized zones either along faults or in areas not related to structure.

Lithologic Mg/Ca ratio maps may facilitate the prediction of cross-folding in the Michigan basin which is not as apparent on structure contour maps.

The author believes that extensive studies of secondary dolomitized zones in limestone formations by accurate chemical analyses, detailed structural contouring, careful interpolation of lithologic Mg/Ca ratio maps, and statistical analyses of resulting data will provide a sound foundation for a better understanding of secondary dolomitization and its relationship to structure and porosity of limestone formations such as the Rogers City.

SUGGESTIONS FOR FURTHER STUDY

For a complete analysis of the relationships existing between secondary dolomitization and porosity and magnitude of structure in dolomitic limestone formation of the central Michigan basin the following suggestions are made:

1. A systematic plan of sampling and analysis of the entire Rogers City formation of Michigan, or any other dolomitized limestone formation with detailed structural contouring and lithologic Mg/Ca ratio maps.
2. A thorough study of the contact between the Rogers City limestone and the Bell shale to determine the nature and extent of a possible unconformity between the two formations.
3. A detailed study of the Bell shale, chemically, structurally and petrographically, may shed more light on the nature of the break between it and the top of the Rogers City limestone.
4. The suggested relationship between dolomite and iron content might be analyzed more carefully for a detailed explanation.

BIBLIOGRAPHY

Adams, J. E. (1934) "Origin, Migration and Accumulation of Petroleum in Limestone Reservoirs in Western United States and Canada," *Problems of Petroleum Geology*, A.A.P.G., p. 359.

Ahrens, L. H. (1950) *Spectrochemical Analysis*, Cambridge, Mass., Addison-Wesley Press,1950,p. 72.

American Public Health Association, Inc. (1955) *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes*, 10th edition, New York.

Anderson, L. L., and Aschenbrenner, B. D. (1954) *Spectrographic Determination of CaO and MgO in Limestone and Dolomite*, Bull. A.A.P.G., Vol. 38, No. 8, 1954, p. 1803.

Apjohn (1838) Journal of Geological Socity of Dublin, Vol. 1, 1838, p. 368.

Banewicz, J. J., and Kenner, C. T. (1952) *Determination of Calcium and Magnesium in Limestones and Dolomites*, Analytical Chem., Vol. 24, No. 7, p. 1186.

Bassett, Charles F. (1935) *Stratigraphy and Paleontology of the Dundee Limestone of Southeastern Michigan*, Geol. Soc. of Am., Vol. 46, p. 425.

Beales, F. W. (1953) *Dolomitic Mottling in Palliser (Devonian) Limestone, Banff and Jasper National Parks, Alberta*, Bull. A.A.P.G., Vol. 37, No. 10, p. 2281.

Beaumont (1836) Bull. Soc. Geol. France, p. 174., cited by Francis M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Bertrand-Geslin (1834) Bull. Soc. Geol. France, Vol. 6, p. 8., cited by Francis M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Bischof (1859) *Elements of Chemical and Physical Geology*, English Translation, Vol. 3, p. 200.

Blackwelder, Eliot (1913) *Origin of the Bighorn Dolomite of Wyoming*, Geol. Soc. of Am., Vol. 24, p. 607.

Boné (1831) Bull. Soc. Geol. France, Vol. 1, p. 115., cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Botha, G. R., and Webb, M. M. (1952) Jour. Inst. Waters Engrs., Vol. 6, p. 459.

Branner (1904) Bull. Mus. Comp. Zool., Vol. 44, p. 264.

Calvin, Samuel (1896) Geology of Cerro Gordo County, Iowa Geol. Survey, Vol. VII, Annual Rep., p. 150.

__________. (1897) Geology of Delaware County, Iowa Geol. Survey, Vol. VIII, p. 120.

Calvin, Samuel, and Bain, H. F. (1899) Geology of Dubuque County, Iowa Geol. Survey, Vol. X, p. 379.

Cheng, Kuang Lu, Kurtz, and Bray (1952) Determination of Calcium, Magnesium and Iron in Limestone, Analytical Chem., Vol. 24, No. 10, p. 1640.

Chilingar, George V. (1956) Relationship Between Ca/Mg Ratio and Geologic Age, Bull. A.A.P.G., Vol. 40, No. 9, p. 2256.

__________. (1956) Use of Ca/Mg Ratio in Porosity Studies, Bull. A.A.P.G., Vol. 40, No. 10, p. 2489.

__________. (1956) Solubility of Calcite, Dolomite, and Magnesite and Mixtures of These Carbonates, Bull. A.A.P.G., Vol. 40, No. 11, p. 2770.

Chilingar, George V., and Terry, Richard D. (1954) Relationship Between Porosity and Chemical Composition of Carbonate Rocks, The Petroleum Engineer, p. 341.

__________. (1954) Simplified Techniques of Determining Calcium and Magnesium Content of Carbonate Rocks, The Petroleum Engineer, p. 368.

Clark, F. W. (1924) The Data of Geochemistry, U.S.G.S. Bull. 770, p. 565.

Claypool, C. B., and Howard, W. V. (1928) Method of Examining Calcareous Well Cuttings, Bull. A.A.P.G., Vol. 12, Pt. 2, p. 1147.

Cohee, G. V. (1948) A Summary of the Stratigraphy of the Southern Peninsula of Michigan, ed. by G. V. Cohee and Helen M. Martin, U.S.G.S. and Mich. Geol. Survey.

Collegno (1834) Bull. Soc. Geol. France, Vol. 6, p. 106., cited by Francis M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Coquand (1841) Bull. Soc. Geol. France, Vol. 12, p. 314., cited by Francis M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Cordier (1862) Compt. Rend., Vol. 54, p. 293., cited by Francis M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Criss, C. R., and McCormick, R. L. (1953) *History and Performance of the Coldwater Oil Field, Michigan*, Petroleum Transactions, AIME.

Daly, Reginald A. (1907) Am. Jour. Science, 4th Series, Vol. 23, p. 93.

__________. (1909) *First Calcareous Fossils and the Evolution of the Limestones*, Bull. Geol. Soc. of Am., Vol. 20, p. 153.

Damour (1851) Annales Chem. Phys., 3rd Series, Vol. 32, p. 362.

Dana, E. S. (1951) *A Textbook of Mineralogy*, John Wiley and Sons, Inc., pp. 516-17.

Dana, J. D. (1843) *Corals and Coral Islands*, Am. Jour. Sci., Vol. 45, p. 120.

__________. (1895) *Mannual of Geology*, 4th edition, p. 134.

Davis, W. M. (1930) *Origin of Limestone* Caverns, Bull. Geol. Soc. of Am., Vol. 41, No. 3, pp. 475-628.

Delanoue (1854) Compt. Rend., Vol. 39, p. 492, cited by Francis M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Dixon (1907) *The Geology of the South Wales Coal Fields*, Part 8: Mem. Geol. Survey, England and Wales, p. 13.

Dixon, W. J., and Massey, F. J. (1951) *Introduction to Statistical Analysis*, McGraw-Hill, New York.

Doelter, and Hoernes (1857) Jahrb. k.-k. ged. Reichsanstalt, Vol. 25, p. 293., cited by Francis M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Douglas, G. V., King, A. M., and Misick, J. D. (1944) Staining Tests for Dolomite, Economic Geol., Vol. 39, No. 1, p. 69.

Eardley, A. J. (1938) Sediments of Great Salt Lake, Utah, A.A.P.G., Vol. 22, No. 10, p. 1305.

Ehlers, G. M., and Radabaugh, R. W. (1937) The Rogers City Limestone, A New Middle Devonian Formation in Michigan, Papers of the Mich. Acad. of Science, Arts, and Letters, Vol. 23, p. 441.

Emmons, S. F. (1886) Monograph, U.S.G.S., Vol. 12, p. 276.

Favre (1879) Compt. Rend., Vol. 28, p. 364, cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Forchhammer, G. (1850) Jour. Parkt. Chemie, Vol. 49, 1850, p. 52, cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Fournet (1849) Bull. Soc. Geol. France, 2nd Series, Vol. 6, p. 502, cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Frapolli (1841) Bull. Soc. Geol. France, Vol. 4, p. 832, cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Geikie (1893) Textbook of Geology, 3rd ed., MacMillan, London, p. 321.

Goulden, C. H. (1952) Methods of Statistical Analysis, John Wiley and Sons, Inc., New York.

Grabau, A. W. (1913) Bull. Geol. Soc. of Am., Vol. 24, p. 399.

__________. (1924) Principles of Stratigraphy, Seiler, New York.

Grandjean (1844) Cited by Bischof, Elements of Chemical and Physical Geology, English Translation, Vol. 3, p. 200.

Green (1876) Jour. Royal Geol. Soc. Ireland, 2nd Series, Vol. 4, Pt. 3, p. 140, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Greiner, H. R. (1956) Methy Dolomite of Northeastern Alberta: Middle Devonian Reef Formation, Bull. A.A.P.G., Vol. 40, No. 9, p. 2057.

Gümbel (1870) Neues Jahrb., p. 753, cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Haidinger (1827) Trans. Royal Soc. Edinburgh, p. 36, cited by Bischof, Elements of Chemical and Physical Geology, English Translation, Vol. 3, 1859, p. 200.

Hall, C. W., and Sardeson, F. W. (1895) Origin of the Dolomites, Bull. Geol. Soc. of Am.,Vol. 6, p. 167.

Hardman (1875-77) On the Carboniferous Dolomites of Ireland, Proc. Royal Irish Acad., 2nd Series, Vol. 2 (Science), p. 705.

Harkness, Robert (1859) On the Jointings in the Carboniferous and Devonian Rocks in the District Around Cork; and on the Dolomites of the Same District, Quarterly Jour. of the Geol. Soc. of London, Vol. 15, p. 86.

Hatch, F. H., Rastall, R. H., and Black, M. (1938) The Petrology of the Sedimentary Rocks, London, Allen and Unwin Ltd., p. 193.

Haussmann (1854) Neues Jahrb., p. 478, cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Heim (1894) p. 505, cited by Zirkel, Lehrbuch der Petrographie, 2nd edition, Vol. 3, p. 503.

Hewett, D. F. (1924) Dolomitization in Southern Nevada, Geol. Soc. of Am., Vol. 35, p. 124.

__________. (1928) Dolomitization and Ore Deposition, Economic Geol., Vol. 23, No. 8, p. 821.

__________. (1931) Geology and Ore Deposits of the Goodsprings Quadrangle, Nevada, U.S.G.S., Professional Paper 162, pp. 57-69.

Högbom (1894) Neues Jahrb., Vol. 1, p. 262, cited by Francis M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Hohlt, Richard B. (1948) The Nature and Origin of Limestone Porosity, Quarterly of the Colorado School of Mines, Vol. 43, No. 4.

Hoppe-Seyler (1857) Zeitschr. Deutsch. Geol. Gesell., Vol. 27, p. 495, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p.251.

Howard, W. V. (1928) A Classification of Limestone Reservoirs, Bull., A.A.P.G., Vol. 12, Pt. 2, p. 1153.

Howard, W. V., and David, M. W. (1936) Development of Porosity in Limestones, Bull. A.A.P.G., Vol. 20, No. 11, p. 1389.

Hunt, T. S. (1859) Am. Jour. of Science, 2nd Series, Vol. 28, p. 382.

Jackson (1843) Am. Jour. of Science, Vol. 45, p. 140.

Jodry, Richard L. (1955) Rapid Method for Determining Magnesium-Calcium Ratios of Well Samples and Its Use in Predicting Structure and Secondary Porosity in Calcareous Fromations, A.A.P.G., Vol. 39, No. 4, pp. 493-511.

Judd, J. W. (1904) The Atoll of Funafuti, cited from Bull. 330, U.S.G.S., p. 487.

Karsten (1849) Archiv. Min., Vol. 22, p. 545, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Keller, W. D., and Moore, G. S. (1937) Staining Drill Cuttings for Calcite-Dolomite Differentiation, Bull. A.A.P.G., Vol. 21, Pt. 2, p. 949.

Knapp, T. S. (1947) A Theory of Rogers City and Dundee Relationships in Central Michigan, Sohio Petroleum Company Report, March, Mt. Pleasant, Mich.

__________. (1950) Reservoir Study of Coldwater Oil Pool, Isabella County, Michigan, Report to Sohio Petroleum Company, unpublished manuscript.

__________. (1956) Discussion of the Section Intervening Between the Top of the Detroit River Evaporites and the Base of the Bell Shale of Central and Western Michigan, Abstract of paper, Staff Geologist, Leonard Oil, Inc., Mt. Pleasant, Michigan.

Knight, Nicholas (1914) Unusual Dolomites, Iowa Acad. of Sci., Proc. 21, p. 127.

__________. (1921) A Chemical Study of Dolomites, Iowa Acad. of Sci., Proc. 28, p. 37.

Krumbein, W. C., and Sloss, L. L. (1951) *Stratigraphy and Sedimentation*, Freeman and Co., San Francisco, Calif., p. 404.

Landes, Kenneth K. (1946) *Porosity Through Dolomitization*, Bull. A.A.P.G., Vol. 30, No. 3, p. 305.

__________. (1951) *Detroit River Group in the Michigan Basin*, Geol. Survey Circular 133.

Lane, A. C., and Seaman, A. E. (1907) *Notes on the Geologic Section of Michigan*, Mich. Geol. Survey, Ann. Report p. 70.

Lauer, A. W. (1917) *The Petrology of Reservoir Rocks and Its Influence on the Accumulation of Petroleum*, Economic Geol., Vol. 12, p. 435.

Lesley (1879) Pa. Second Geol. Survey, Rept. M.M., p.311.

Leymerie (1864) Memories de L'Academie Imperiale des Sciences de Toulouse, 6th Series, Vol. 2, p. 307, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Linck (1909) Monatsh. Deutsch. geol. Gesell., p. 230, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Lindgren, Waldemar (1912) *The Nature of Replacement*, Economic Geol., Vol. 7, pp. 521-35.

Lloyd, E. Russell (1929) *Origin of Porosity in Reef Limestone or Dolomite*, Bull. A.A.P.G., Vol. 13, No. 9, p. 1219.

Lockett, J. R. (1947) *Development of Structures in Basin Areas of Northeastern United States*, Bull. A.A.P.G., Vol. 31, No. 3, p. 429.

Loretz (1878) Zeitschr. Deutsch. geol. Gesell., Vol. 30, p. 387, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Ludwig, and Theobold (1852) Pogg. Annalen, Vol. 87, p. 91, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Mellor, J. W. (1932) *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 12, Longmans, Green, and Co., New York, p. 547.

Michael (1904) Zeitschr. Deutsch. geol. Gesell. Prot., Vol. 56, P. 127, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p.251.

Mojsisovics (1879) Die Dolomitriffe von Süd Tirol, p. 505, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Morlot (1847) Haidinger's Naturw., Abh. Vol. 1, p. 305, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Murray, A. N. (1930) Limestone Oil Reservoirs of the North-eastern United States, and of Ontario, Canada, Economic Geol., Vol. 25, p. 452.

Murray, and Hjort (1912) The Depths of the Ocean, p. 180, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Nadson, and Walther (1916) Gesichte der Erde und des Lebens, cited in Science, Vol. 44, p. 90.

Nahnsen (1913) Neues Jahrb., Beil. Bd. p. 277, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Nauck (1848) Pogg. Annalen, Vol. 75, p. 129, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Newcombe, R. B. (1930) Middle Devoian Unconformity in Michigan, Bull. Geol. Soc. of Am., Vol. 41, p. 725.

Orton, Edward (1888) The Geology of Ohio, Considered in Its Relations to Petroleum and Natural Gas, Geol. Survey of Ohio, Vol. 6, p. 307.

Peach, and Horne (1907) The Geological Structure of the Northwest Highlands of Scotland: Mem. Geol. Survey, Great Britian, p. 370.

Peppel, S. V. (1906) Technology of the Lime Industry, Bull. 4, Ohio Geol. Survey, p. 252.

Pettijohn, F. J. (1949) Sedimentary Rocks, Harper, New York.

Pfaff, F. W. (1894) Neues Jahrb. Beil. Bd. 9, p. 485, cited by F. M. Van Tuyle, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Phillipi (1907) Neues Jahrb., Festband, Vol. 1, p. 307, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Pirsson, L. V., and Knopf (1949) *Rocks and Minerals*, John Wiley and Sons, Inc., pp. 262-268.

Raymond, Percy E. (1925) *A Possible Factor in the Formation of Dolomite*, Geol. Soc. of Am., Vol. 36, p. 168.

Rich, John L. (1938) *Discussion*, Bull. A.A.P.G., Vol. 22, No. 7, p. 918.

Robinson, W. I. (1924) *Petroliferous Formations,* Mich. Geol. Survey, p. 4, unpublished manuscript.

Rodgers, J. (1955) *Terminology of Limestone and Related Rocks, an Interim Report*, Jour. Sed. Petrology, Vol. 24, No. 4, p. 225.

Salomon (1908) Abh. k.-k. geol. Reichsanstalt, Vol. 21, Part I, p. 408, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p.251.

Sandberger (1845) Neues Jahrb., p. 577, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Scheerer (1866) Neues Jahrb., p. 1, cited by F.M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol.25, 1914, p. 251.

Schmidt (1875) Trans. St. Louis Acad. Science, Vol. 3, No. 2, p. 246.

Schwarzenbach, G., and Ackermann, H. (1947) *Ethylenediaminetetraacetic Acid*, Helvet. Chim. Act, 30, p. 1798, cited from *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes*, Am. Public Health Assoc., 1955.

Schwarzenbach, G., Biedermann, W., and Bongerter, F. A. (1946) *A New Simple Titration for the Determination of Water Hardness*, Helvet. Chim. Acta, 29, p. 811, cited from *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes*, Am. Public Health Assoc., 1955.

Scowler (1838) Jour. of Geol. Soc. of Dublin, Vol. 1, p. 382, cited by F. M. Van Tuyl, *The Origin of Dolomite*, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Skeats, E. W. (1902) Bull. Mus. Comp. Zool., Vol. 42, p.53.

Skeats, E. W. (1905) *On the Chemical and Mineralogical Evidence as to the Origin of the Dolomites of Southern Tryol*, Quarterly Jour. of the Geol. Soc. of London, Vol. 61, p. 97.

__________. (1918) *The Formation of Dolomite and its Bearing on the Coral Reef Problem*, Am. Jour. of Sci., 195, p. 188.

Sloss (1946) *Spectrochemical Sample Logging of Limestone*, Bull. A.A.P.G., Vol. 30, No. 11, p. 1888.

Smith, R. A. (1915) *Limestones of Michigan*, Mich. Geol. and Biol. Survey, Publ. 21, Geol. Series 17, p. 120.

Sorby (1856) *Influence of Magnesium Sales in Solution in Sea Water as Dolomitizing Agents*, Report of British Assoc., Trans. of Sections, p. 71.

Spurr (1898) *Geology of the Aspen Mining District, Colorado*, Monograph, U.S.G.S., Vol. 31, p. 210.

Stauffer, C. A., and Thiel, G. A. (1933) *The Limestones and Marls of Minnesota*, Minn. Geol. Survey Bull. 23, p. 17.

Steidtmann, Edward (1911) *The Evolution of Limestone and Dolomite*, Jour. of Geol., Vol. 19,p.323.

__________. (1916) *Results of a Study of Dolomitization*, Science, New Series, Vol. 44, p. 56.

__________. (1917) *Origin of Dolomite as Disclosed by Stains and Other Methods*, Bull. Geol. Soc. of Am., Vol. 28, p. 431.

Stout, Wilber (1941) *Dolomites and Limestones of Western Ohio*, Geol. Sur. of Ohio, Bull. 42, p. 9.

Suess (1906) *The Face of the Earth*, English Translation, Vol. 2, p. 262.

Taras, M. (1948) *Photometric Determination of Mg in Water with Brilliant Yellow*, Anal. Chem. 20, p. 1156.

Tarr, W. A. (1919) *Contribution to the Origin of Dolomite*, Geol. Soc. of Am., Vol. 30, p. 114.

__________. (1920) *A Possible Factor in the Origin of Dolomite*, Science, Vol. 51, p. 521.

Thiel, G. A., and Sherman, G. D. (1938) Dolomitization in Glacio-Lacustrine Slits of Glacial Lake Agassiz, Geol. Soc. of Am., Vol. 49, No. 12, Pt. 2, p. 1903.

Ulrich, and Schuchert (1901) New York State Museum, Bull. 52, p. 633.

Van Hise (1904) Monograph, U.S.G.S., Vol. 47, p. 803.

Van Tyle, Francis M. (1914) The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, p. 251.

__________. (1915) New Points on the Origin of Dolomites, Abst., Geol. Soc. of Am., Vol. 26, p. 62.

__________. (1916) New Points on the Origin of Dolomites, Am. Jour. of Sci., Vol. 192, Series 4., 42, p. 256.

__________. (1916) The Present Status of the Dolomite Problem, Science, New Series, Vol. 44, p. 688.

Van Tuyl, F. M., Parker, B. H., and Skeeters, W. W. (1945) The Migration and Accumulation of Petroleum and Natural Gas, Colorado School of Mines Quarterly, Vol. 40, No. 1, p.34.

Vishnyakov, S. G. (1955) Genetic Types of Dolomite Rocks, Doklady Akad. Nauk SSSR, Tom 76, No. 1, p. 112, cited by Chilingar, Use of Ca/Mg Ratio in Porosity Studies, Bull. A.A.P.G., Vol. 40, No. 10, p. 2489.

Vogt (1898) Zeitschr. Prakt. Geologie, p. 4, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Von Buch (1847) Cited by Morlot, Haidinger's Naturw., Abh. Vol. 1, p. 305.

Von Richthofen (1905) Cited from E. W. Skeats, Quarterly Jour. Geol. Soc. of London, Vol. 61, p. 97.

Wagner (1839) Cited by F. Pfaff, Pogg. Annalen, p. 465.

Wallace (1913) Jour. Geol., Vol. 21, p. 402.

Walther (1908) Geschichte der Erde und des Lebens, p. 90, cited by F. M. Van Tuyl, The Orgin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Weaver, Paul (1946) The Formation of Evaporites Under Marine Evaporation Conditions, Bull. A.A.P.G., Vol. 30, No. 11,p. 1965.

Weigelin (1913) Neues Jahrb., Beil. Bd. 35, p. 628, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

Weller, Stuart (1911) Are the Fossils of the Dolomites Indicative of Shallow, Highly Saline and Warm Water Seas?, Geol. Soc. of Am., Vol. 22, p. 231.

Whiteside, Robert M. (1932) Geologic Interpretations from Rotary Well Cuttings, A.A.P.G., Vol. 16, No. 7, p. 653.

Wichmann (1909) Zeitschr. Deutsch. geol. Gesell., Vol. 61, p. 392, cited by F. M. Van Tuyl, The Origin of Dolomite, Iowa Geol. Survey, Vol. 25, 1914, p. 251.

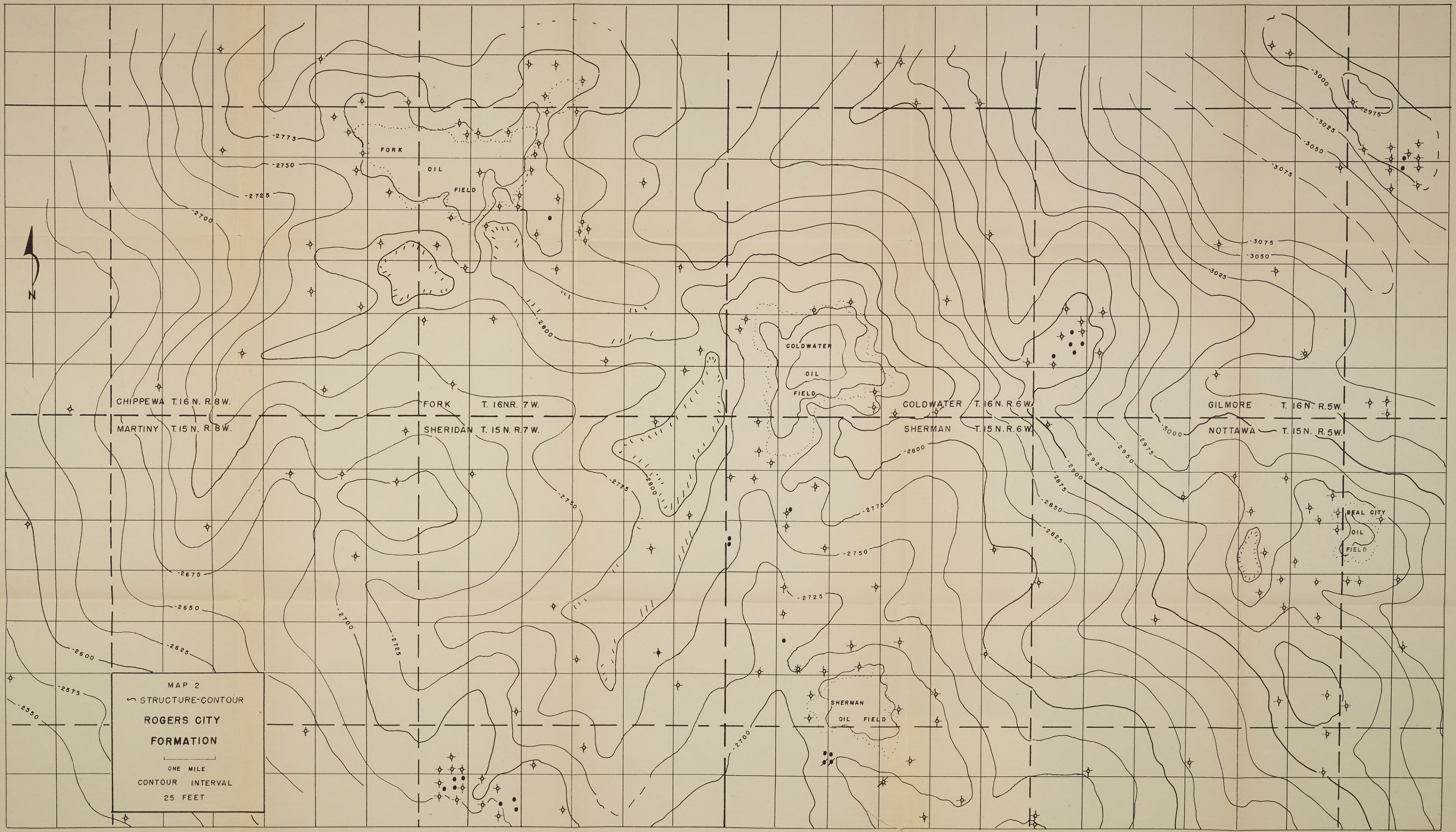
Wissmann (1859) Cited by Bischof, Elements of Chemical and Physical Geology, English Translation, Vol. 3, p. 200.

Young, Robert T. (1955) Significance of the Magnesium/Calcium Ratios as Related to Structure in the Stony Lake Oil Field, Michigan, unpublished Master of Science Thesis, Dept. of Geology, Michigan State University.

Zirkel (1894) Lehrbuch der Petrographie, 2nd ed., Vol. 3, p. 503.

Pocket has: Map 2
Map 3
Map 4

/③



MAP 2

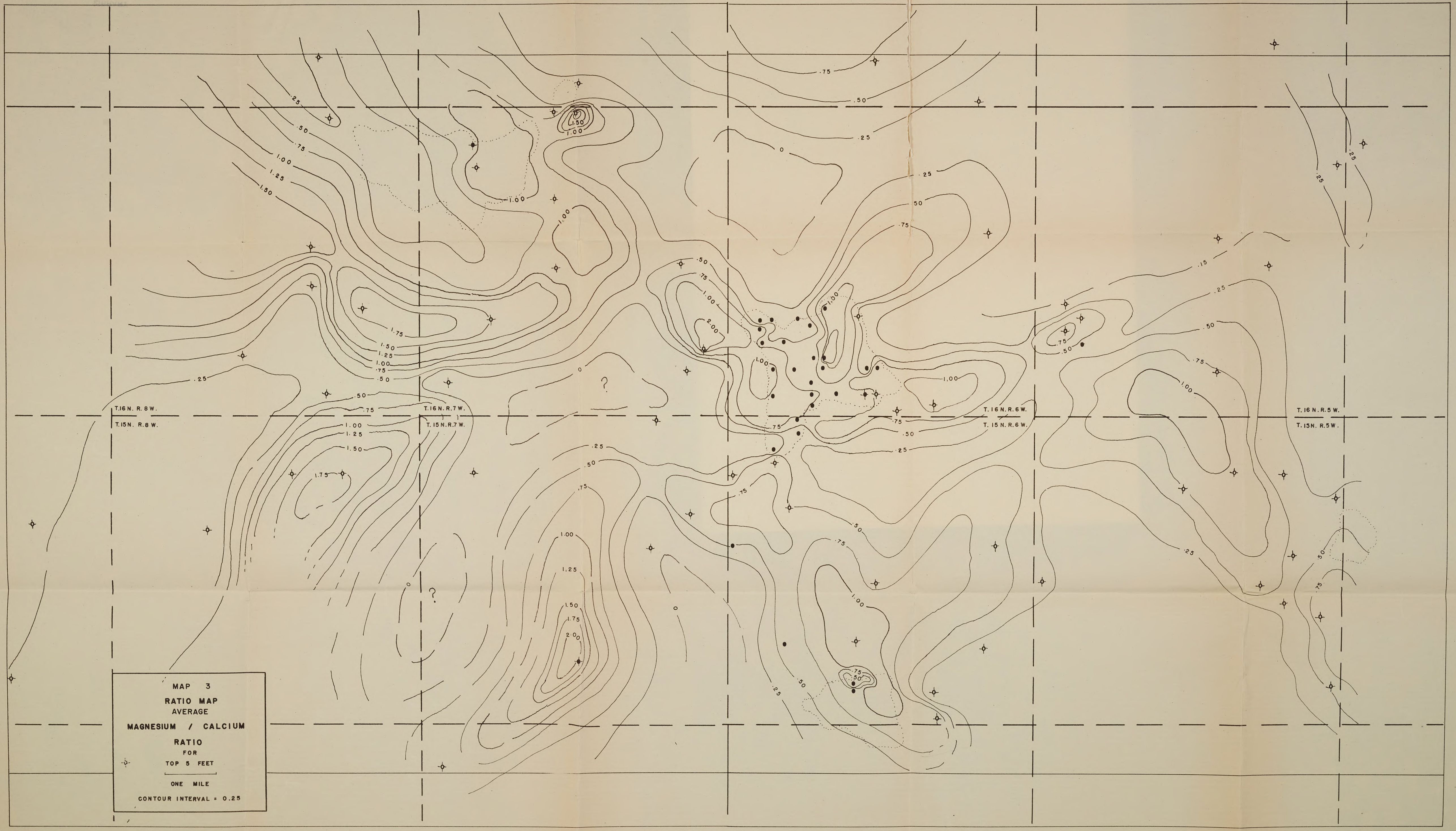
STRUCTURE-CONTOUR

ROGERS CITY FORMATION

ONE MILE

CONTOUR INTERVAL

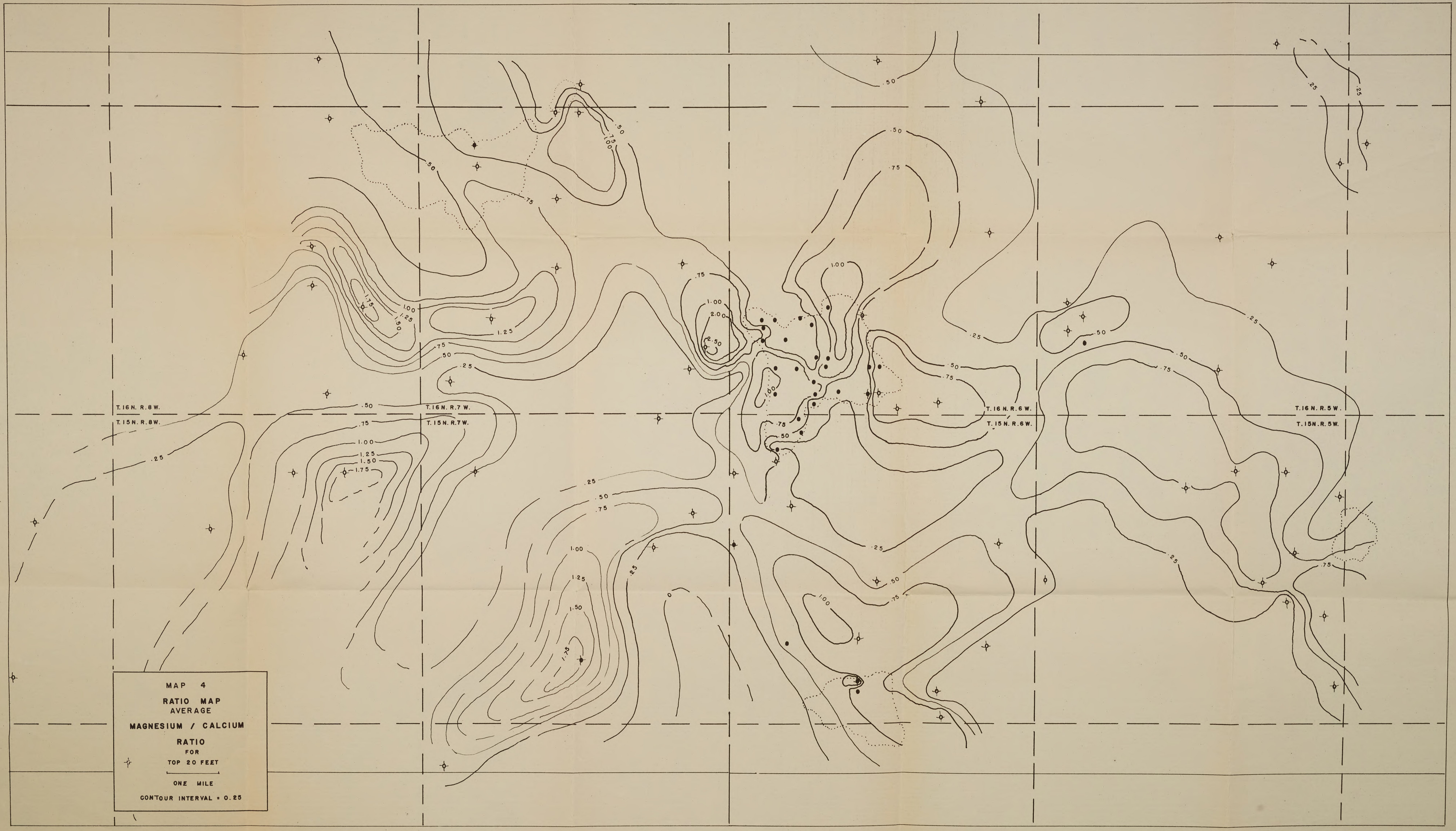
25 FEET



MAP 3
RATIO MAP
AVERAGE
MAGNESIUM / CALCIUM
RATIO
FOR
TOP 5 FEET

ONE MILE

CONTOUR INTERVAL = 0.25



MAP 4

RATIO MAP
AVERAGE

MAGNESIUM / CALCIUM

RATIO
FOR
TOP 20 FEET

ONE MILE

CONTOUR INTERVAL = 0.25