A CHEMICAL AND PETROGRAPHIC ANALYSIS OF WOODEN No. 6 WELL; MIDDLE ORDOVICIAN FROM HILLSDALE COUNTY, MICHIGAN

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By

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ABSTRACT.

A CHEMICAL AND PETROGRAPHIC ANALYSIS OF WOODEN No.6 WELL, MIDDLE ORDOVICIAN FROM HILLSDALE COUNTY, MICHIGAN.

By L. Olayinka Asseez

Oil and gas showings and production in the Ordovician limestones of Michigan are restricted to areas where the Trenton - Black River sequence is partially or completely dolomite. In 1957 Tinklepaugh observed that there is a correlation between structure and epigenetic dolomitization- the highest degree of dolomitization being attained in the anticlinal crests.

In an attempt to separate diagenetic from epigenetic dolomite in the Ordovician system in the Albion-Scipio field areas, Dr. C.E.Prouty started the first part of a series of studies in 1961. On the first well core, the Peterson-Howard No.1, Hamil (1961) studied the vertical Ca/Mg variation, Kirschke (1961) the petrographic analysis and Zaitzeff (1962) the microfossil analysis.

In this second part of the investigation, the writer studied the Wooden No.6 well, Hillsdale County, Michigan.This study consisted of:

1. Detailed chemical analysis using Versenate method.
2. Insoluble residue analysis,
3. Staining, using potassium ferricyanide and
4. Thin sections, of Trenton limestone.

An attempt was made to correlate the Mg/Ca ratios and the results of the insoluble residues with the radioactive logs. The common association of abundant dolomite with shale was noted and four reasons were

suggested for this common occurrence.

The writer believes that there are two periods of dolomitization-early and late. These two types occur together although one type may be more dominant than the other in any particular horizon. The writer feels that future work would not be able to separate them completely since there is often no clear-cut stratigraphic boundary between them.

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ACKNOWLEDGEMENTS

The writer is deeply indebted to Dr. C.E. Prouty under whose direction the problem was undertaken and without whose many suggestion this work could not have attained its present standard,

He is also grateful to Dr. J.W.Trow and Dr. H.B.Stonehouse, both members of the guidance committee, for their helpful support.

Dr. B.G. Ellis of the Soil Science Department, James Lammons and Daniel Robbins of the Geology Department were also very helpful with the many unsolved problems of the differential thermal analysis machine.The writer is very grateful to them all.

The Davis Drilling Company Inc. deserve the writer's unqualified gratitude for supplying the well core which made this study possible. It is hoped the company will always support the department in this and many other ways.

INTRODUCTION

The Trenton limestone normally has low effective porosity except where dolomitization has led to increased porosity and permeability. Hence some oil and gas prospecting has been based on the lateral variation in the calcium /magnesium ratio, with a hope of determining the limit of the Albion-Scipio structures. However little attempt has been made to determine how much of this variation is stratigraphic.

This led Dr. C.E.Prouty to the feeling that if the vertical variation of calcium/magnesium ratio was determined, and the paleontologic and petrographic characters of several wells were known, we might be able to separate epigenetic from stratigraphic dolomitization. The first three parts of this problem were conducted on the Peterson-Howard No.1 Well (Hamil 1961, Kirschke 1962 and Zaitzeff 1962) located in Pulaski Township, Jackson County (section 17, T 4 S, R 3 W) .

In an attempt to contribute to the solution of this very important problem, the writer undertook the chemical, staining, petrographic and thermal analyses of the second core, the Wooden No. 6, located in Hillsdale County just southwest of the structural trend of the Albion-Scipio field (section 4, T 5 S, R 3 W, Fig. 1.) The top of the Trenton was intersected at 3562' but coring was not started until 3765, and was stopped just short of the Black River at 3915'.

The writer had hoped to be able to co-ordinate all the aspects of his studies and especially to compare the thermal and chemical results. However the thermal program was reluctantly abandoned after he had failed to make the differential thermal analysis machine work.

It is hoped that more wells will be available and that other interested students will carry this problem to its logical conclusion.

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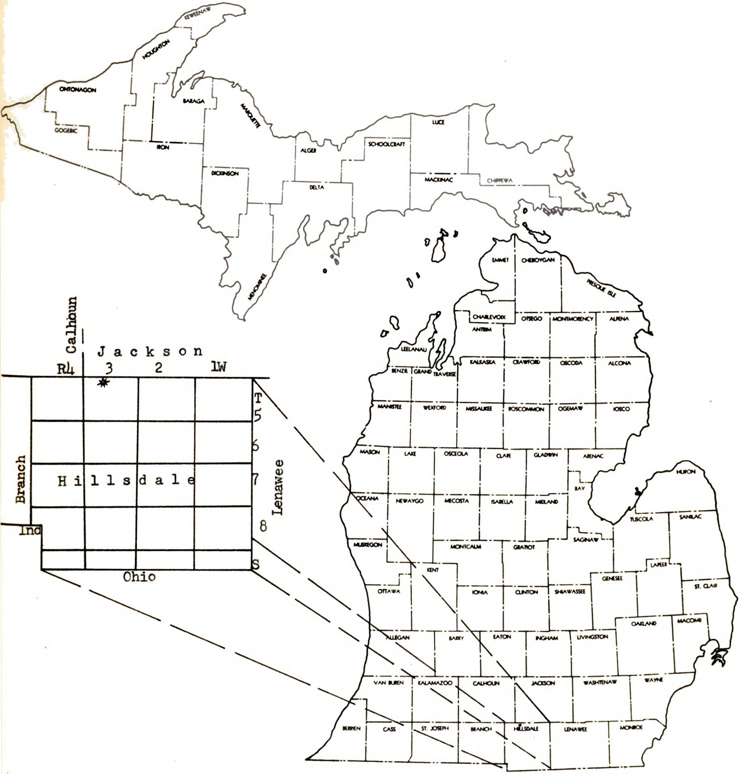
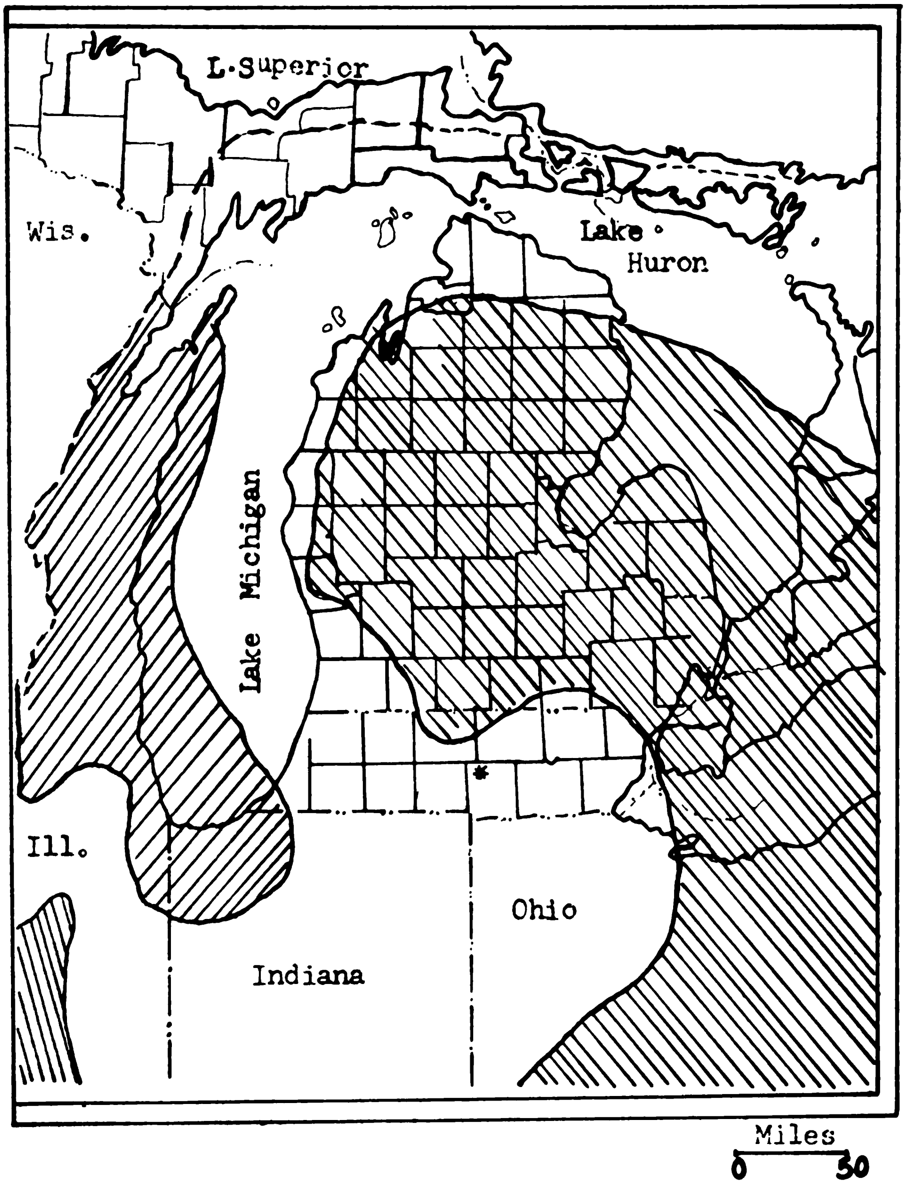
Fig.1. Location of Wooden No.6 well.





Entirely Dolomite

Limestone and Dolomite

Entirely Limestone

Boundary of Trenton and Black River at surface.

* Location of Wooden No.6 well.

Fig.2 Lithology of Middle Ordovician Rocks

(modified after Cohee , G.V.1947)

GENERAL STRATIGRAPHY

Lower Ordovician

The lower Ordovician rocks of Michigan consist of the Oneota dolomite, the Richmond sandstone and the Shakopee dolomite (Table 1). The Oneota is a buff or brown dolomite with little green shale and may be cherty, sandy and oolitic in places. In the southwestern parts of Michigan where it is over 300 feet thick, it is largely sandstone with surbordinate dolomite. The New Richmond sandstone is thin and underlies the buff, brown or gray Shakopee dolomite. This dolomite has thin beds of shale and is cherty or sandy in places.

Middle Ordovician

The Middle Ordovician rocks consist of the St.Peter sandstone,the Glenwood shale, the Black River limestone and the Trenton limestone. The basal St. Peter sandstone is white to brown, very pure, friable and has chert fragme ts and pyrite crystals in places.It is well sorted, well rounded ,frosted (Horowitz 1961) and unconformably overlies the lower Ordovician rocks in the southeastern parts where the Prairie du Chien has been eroded.

The Glenwood shale consists chiefly of fine grained sandstone, shaly dolomite and is 10-100 feet thick. In the southeast of Michigan, a green ,brown, pyritic sandy shale underlies the Black River where the St. Peter has been eroded. This shale is lithologically similar to the Glenwood formation although it may not be the exact time equivalent of the Glenwood farther to the west (Cohee, 1948).

The Black River and the Trenton limestones are generally brown,gray crystalline limestone and dolomite in varying proportions (Fig.2). Dolomite is predominant in the eastern parts of the Michigan Basin,

Period	Epoch	System	Series	Group	Formation	Member
ORDOVICIAN	Late	ORDOVICIAN	CINCINNATIAN	RICHMOND	Queenston	
					Utica	Collingwood
	Middle		MOHAWKIAN	TRENTON	Groos Quarry	
					Chandler Falls	
				BLACK RIVER	Bony Falls	
	Early		CHAZYAN			Glenwood
					St.Peter Ss.	
			CANADIAN	PRAIRIE DU CHIEN	Shakopee dol.	
					New Richmond	
					Oneota dol	
CAMBRIAN	Late	CAMBRIAN	ST. CROIXAN	LAKE SUPERIOR	Trempealeau	Jordan Ss.
						Lodi
						St.Lawrence
					Munising	Franconia Ss.
						Dresbach
						Eau Claire
						Mount Simon
	Middle				Jacobsville Ss.	
	Early					

Table 1. Generalized Section of the Cambrian and Ordovician Systems of Michigan. (modified after Mich. Geol.Survey, Chart 1,1964)

limestone in most parts of central Michigan, and limestone and dolomite in northeastern Illinois, northwestern Indiana and along the Kankakee and Findlay arches. The occurrence of dolomite along major anticlinal axes is strongly suggestive of a secondary origin, possibly related to folding (Cohee 1948).

The base of the Trenton limestone in southwestern Ontario consists of argillaceous limestone and shale about 400 feet below the Trenton and is easily traced into Michigan , except in Berrien County where it is largely dolomite (Cohee, 1948). The base is distincly identifiable on the neutron log at 3920 feet.

The maximum thickness of the Black River and Trenton limestone is attained in eastern Michigan and the adjoining areas of Ontario where they are over 900 feet. The structural thickening in the Chatham sag has led Cohee (1948) to suggest that it was a structurally low area that served as the link between the Michigan Basin and the seas on the east in Black River time. The Black River and Trenton thin very considerably over the adjoining arches.

Upper Ordovician

The upper Ordovician formations attain a maximum thickness of 800 feet in the southeast - close to the area of greatest thickness of Middle Ordovician formations. Largely they consist of dark gray shale with minor amounts of dolomite and limestone, and comprise chiefly the Utica, Lorraine and Queenson shales.

The Utica is a dark gray to black shale 150-200 feet thick and is overlain by the Lorraine,a dark gray calcareous shale, with thin beds of limestone and dolomite, and is 290-390 feet thick. The Queenston shale is predominantly red with interbedded limestone or dolomite and is up to 200 feet thick in places.

LABORATORY TECHNIQUES

Sampling

Using a diamond rock saw, a relatively thin slice was made from each piece of core whose top had been carefully marked. It was necessary to number each of the pieces,(the top being No. 1) in each core box. This made it easy to align several pieces together for comparative purposes.

After all the slices had been made, they were bagged at two-foot intervals and each bag was carefully labelled. Each sample was then pulverized in a Denver jaw crusher and later ground finer in a steel motar. It was then split into several parts (Krumbein & Pettijohn 1938)until about one eighth of the sample was left. This was finally pulverized in a steel mortar, sieved in a 0.417 mm Tyler sieve, bottled and then labelled.It was believed that by preparing the samples this way, each would be representative of the two-foot interval which Rones (1955) has shown to be optimum.

Chemical Analysis.

Digestion:

1. The sample was washed, dried and one gram of it weighed into a 250 ml. flask, followed by 10 ml. of perchloric acid.
2. It was heated gently until the solution turned colorless after which it was evaporated to dryness.
3. The cooled residue was dissolved in 3 ml. of 50% hydrochloric acid and 10 ml.of distilled water. The residue was filtered off and the solution was diluted to 250 ml.

It is essential that all work be done under the hood and as cautiously as possible since perchloric acid is very explosive and also has very poisonous fumes. It is also very important that distilled water be used to make solutions and to rinse apparatus after washing owing to the high amount of dissolved inorganic materials in tap water.

Determination of Calcium:

The analytical method used herein is that proposed by K.L.Cheng, et al (1952).

Versenate Solution. Dissolve 4 grams of the disodium salt of ethylene -dinitrilo tetra-acetic acid in one liter of water. Standardize the solution against a standard calcium solution as described below.

Standard calcium solution. Dissolve 2.5 grams of reagent grade of calcium carbonate in about 5 ml. of 50% hydrochloric acid and dilute exactly to one liter with water. This solution contains one milligram of calcium per milliliter.

Potassium hydroxide. Use a 20% aqueous solution.

Calcium indicator powder. Mix thoroughly 40 grams of powdered potassium sulfate and 0.2 gram of murexide.

Titration:

1. Pipette a 10 ml. aliquot of the solution to be analysed into a 200 ml. porcelain dish; add approximately 20 ml. of water, one ml. of potassium hydroxide and a tiny scoop of of the prepared calcium indicator powder.
2. Stir and titrate with the standard Versenate until the color of the solution changes from pink to violet.

Determination of Magnesium:

Buffer solution. Dissolve 60 grams of ammonium chloride in about 200 ml. of water, and add 570 ml. of concentrated ammonium hydroxide. Dilute to 1 liter with water.

Potassium cyanide. Prepare a 10% solution.

<u>F-241 indicator</u>. Dissolve 0.15 gram of Erichrome black T (F-241) and 0.5 gram of sodium borate in 25 ml of metanol.

Titration:

1. Pipette a 10 ml aliquot of the solution to be analysed into a 200 ml porcelain dish, add 25 ml. of water, 2 to 3 ml. of buffer solution, a few drops of potassium cyanide solution and about 8 drops of F-241 indicator.
2. Stir and titrate with Versenate solution until the solution changes from wine red to clear blue.

For faster and more consistent results the above solutions were mixed before titration as follows;

For magnesium combine the buffer solution, water and potassium cyanide in the ratio of 3: 26: 1, and use 30 ml of this solution for titration. For calcium, mix a certain quantity of potassium hydroxide solution with twenty times its volume of water and use 20 ml of this solution for titration.

Each sample was titrated three times and the average of the readings was used in calculation.

Calculation:

Since 1 gram of the sample is made upto 250 ml.solution and 10 ml.of this aliquot is used for titration, we have:

$$\frac{A \times 25 \times 1.4 \times B}{1000} \times 100 = \text{percent calcium oxide.}$$

$$\frac{C \times 25 \times 1.66 \times (D-B)}{1000} \times 100 = \text{percent magnesium oxide.}$$

A = milligrams of calcium per ml.of Versenate solution.

C = milligrams of magnesium per ml. of Versenate solution.

B = milliliters of Versenate solution used in titration for calcium using murexide as indicator.

D = milliliters of Versenate used in titration for magnesium using F-241 as indicator.

Standardization with standard calcium solution:

As prepared the calcium solution contains 1 milligram of calcium per ml•of solution; 25.5 ml. of Versenate was needed to titrate 10 ml of this solution to its end point.

10 milligrams of calcium (solution)   25.5 ml Versenate

Versenate = 10 mg Ca / 25.5 ml. =0.40 mg ('A' of Equation)

To compute the milligrams of magnesium per ml. of Versenate we use the figure as follows:

$$\frac{\text{Atomic weight of Mg}}{\text{Atomic weight of Ca}} = \frac{24.32}{40.08} = 0.607$$

Versenate = 0.40 x 0.607 = 0.242 mg /ml. Versenate ('C' of Equation.)

This basic formula permits computations without using exactly 1 gm. of the sample , and without standardizing the Versenate solution for either calcium or magnesium, although these were done in this investigation. Recent work (R.L.Jodry 1961) in the Research and Development Division of the Sun Oil Company has produced two curves - Figs. 3 & 4. Figure 3 may be used to compute the magnesium /calcium ratio by dividing the milliliters of Versenate used to titrate for calcium by the milliliters used to titrate for magnesium, and locating this point on the vertical axis and then reading down to obtain the ratio on the horizontal scale at the bottom of the curve. This solves the equation graphically.

It has also been shown that the ratio calculated from the basic formula needs to be corrected for a slight error in the formula due to an inherent error in the chemical reaction— the inability to differentiate exclusively between calcium and magnesium. The calculated ratio is located on the vertical scale of Fig.4 and the true ratio is read off on the horizontal scale. The basic formula corrected in this way gives the same

Fig.3. Diagram for Calculating Mg/Ca Ratios from volumes of Versenate Used in Titrations.

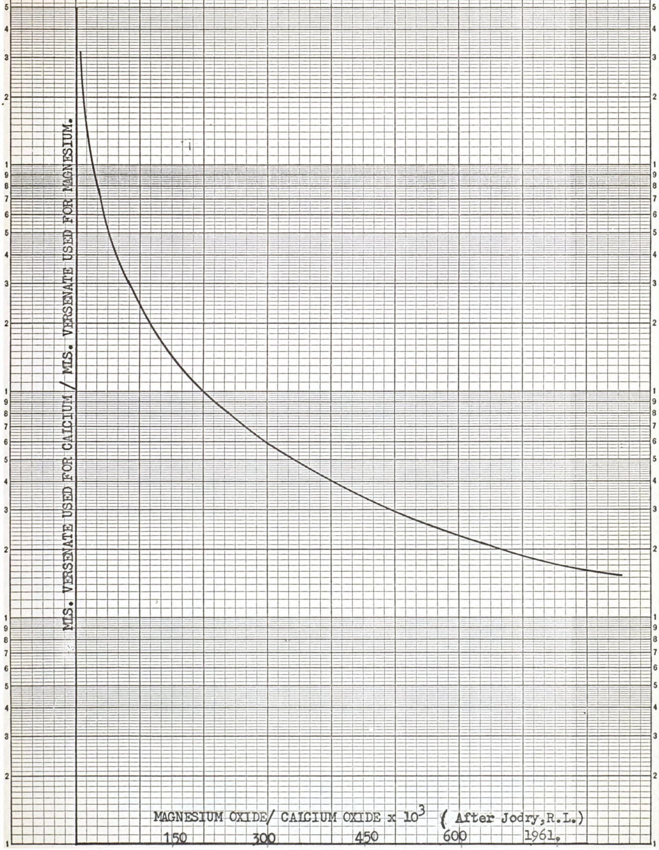
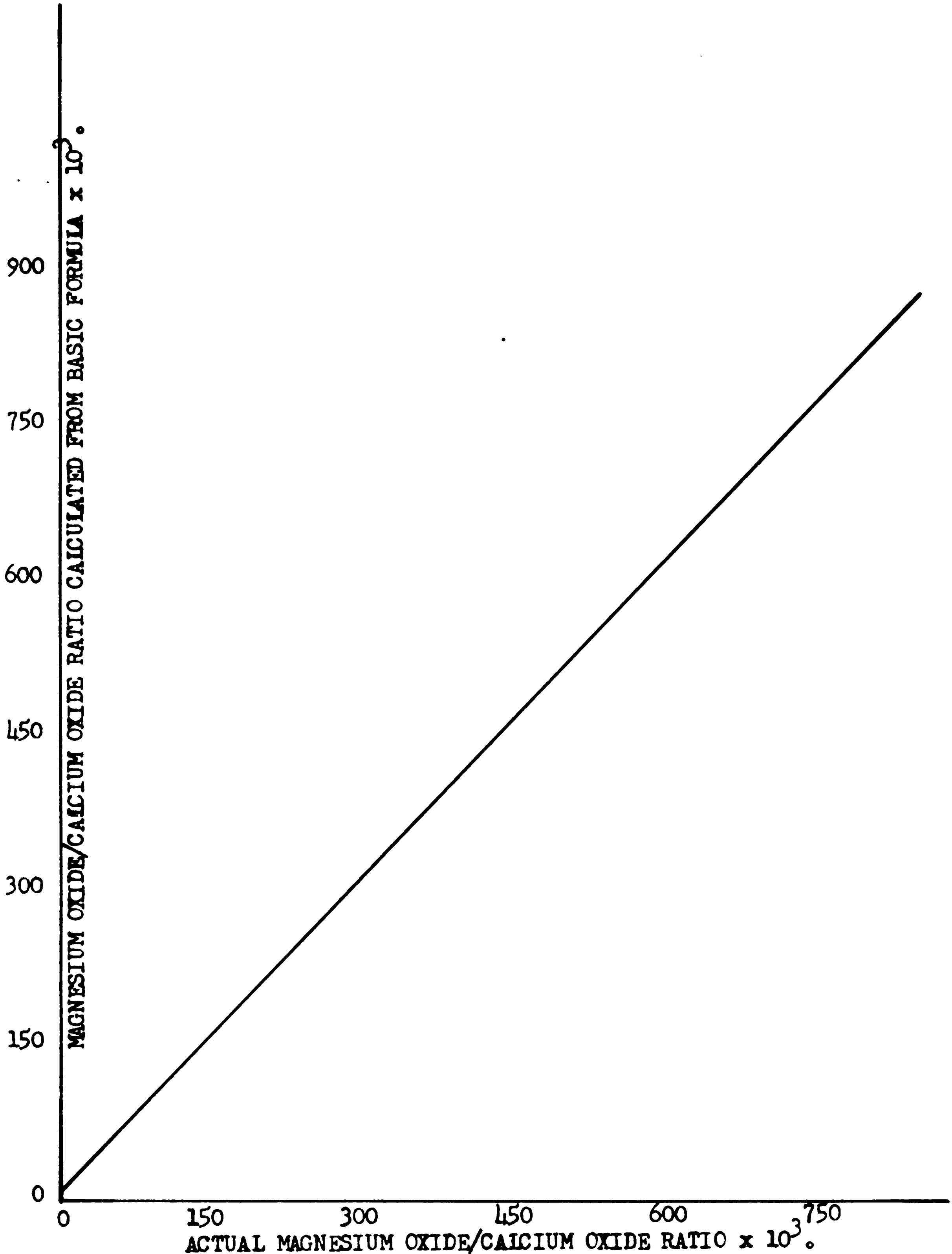


Fig.4. **Diagram for Correcting Calculated Ratios.**



(After Jodry, R.L. 1961)

ratio as that calculated from Fig.3, but the writer used the formula corrected by Fig. 4 since he was also seeking the percentage composition of calcium and magnesium.

The writer has found it easier to work with Mg/Ca ratio since small changes in magnesium become accentuated. It also produces a ratio varying from 0.00 for limestones to 0.6 for dolomites and minimizes changes in predominantly calcitic rocks. On the other hand, variation in the Ca/Mg ratio is from 0.6 for dolomites to infinity for limestones, thus making graphical representation impractical. It also emphasises small changes in predominantly calcitic rocks. The writer has included this ratio in Table 2 because it might be useful for comparative purposes with Hamil (1961) who used it in his work.

Insoluble Residues.

1. 1 gram of the sample prepared for the chemical analysis was put in a weighed test-tube and three or four drops of 4% hydrochloric acid were added. A few more drops were added (three drops at a time) after the effervescence had stopped.

The samples were left overnight after which they were centrifuged and the clear liquid on top was decanted.

2 . More acid was added and the process repeated until there was no reaction when fresh drops of acid were added.Each sample was left in the acid for two to three hours where it was not necessary to leave it overnight.

3. The residue was washed three times, oven dried, cooled and weighed. The difference in weight represents the weight of the insoluble materials.

Staining.

The process of staining employed in this investigation was that developed by Steidman (1917). This method stains dolomite blue when the sample is immersed in a solution of potassium ferricyanide and depends on the presence of ferrous oxide in the dolomite. This ferrous oxide reacts with the ferricyanide to give the blue color.Calcium remains unaffected.

The sliced surface of each piece of core was immersed in a 5% solution of hydrochloric acid to which a few drops of concentrated solution of potassium ferricyanide had been added.Each piece was supported on two small balls of wire gauze so that the submerged surface did not rest on the bottom of the container.

Each sample was immersed in the solution for two to three minutes at first, but the time was increased as the solution became weaker.The solution was changed after the fourth set of samples had been stained. This process produced excellent relief in the unstained parts and hence identification was relatively easy.

The stained surfaces were then observed under the binocular microscope with a view of determining:

1. Distribution, nature, and amount of dolomite.
2. Distribution, nature and amount of insoluble residues.
3. Fossils.
4. Texture.
5. Diagenetic changes.
6. Relation of insolubles and dolomite to bedding.

In addition to these records, a diagram of the stained surface was made in order to give a better picture of the stained surface to the reader. It was not possible to use conventional lithologic symbols because each lithologic type was drawn as close as possibe to its true position. In a section one inch thick and using the same scale as in this investigation, (1" = 1') it was not feasible to use these

symbols. With the approach used in this investigation it was much easier.

Preparation of Thin Sections

While the megascopic descriptions were being made, portions of the core from which thin sections would be made were marked with a marking pencil and numbered. The position of each marked section was located on the columnar section with the appropriate number. This portion was made so that the long axis was perpendicular to bedding, and the top was marked by an arrow.

When all the selections had been made, thin slabs about 1/16 of an inch thick were cut. These were stored until all the slabs had been cut. Each slab was then ground for a few minutes on a lap wheel with 600 carborundum to provide a flat smooth surface for mounting. This surface was then stained in a strong solution of potassium ferricyanide to which a few drops of 5% hydrochloric acid had been added.

The slab and the glass slide, which had first been frosted with No. 180 grit, were laid on a heated metal plate with the clean side of the slab and the frosted side of the slide turned up. The flame of the bunsen burner was adjusted so that the aroclor did not melt too rapidly when applied to the heated slide. When most of the bubbles had been 'cooked' out, the glass slide and the slab were removed. The slab was then gently placed, one side first, on the slide and the excess aroclor gradually worked out as the slab settled into place. By gently pressing down with the eraser of a pencil, most of the bubbles and excess aroclor were worked out. The slide was then labelled by means of a diamond pencil.

Each of the mounted slabs was then ground on a lap wheel using No. 180 carborundum to about 0.03 mm thickness. Grinding was then transferred successively to other lap wheels using Nos. 4000, 6000 and 8000. Final grinding was done by hand on a glass plate with No. 800 powder until the desired thinness was attained.

The finished sections were then immersed in a strong solution of potassium ferricyanide to which a few drops of 3% hydrochloric acid had been added. The slides were taken out of the staining solution after about six hours. They were then studied for fabric, composition, occurrence and nature of dolomitization.

Although this test involves the recognition of the presence of iron, it is recognized that dolomitization and iron content are related, and so this is a recognized staining test for dolomite. The good correlation (pp.26-42) of chemical analyses and stain observation in this work justifies its application. A notable exception occurs between 3801.5 and 3805.3, where the magnesium content observed from chemical analyses is very much lower than would be expected from the observation of the stained surface.

OBSERVATIONS AND RESULTS

Classification of limestones based on Ca/Mg Ratio:

The following classification was proposed by G.V. Chilingar (1957) and is based on Ca/Mg ratios. The writer has adopted the same classification in order to make room for easy comparison of all past and future investigations in this program.

	Ca/Mg Ratio
Magnesian dolomite	1.0 - 1.5
Dolomite	1.5 - 1.7
Slightly calcareous dolomite	1.7 - 2.0
Calcareous dolomite	2.0 - 3.5
Highly dolomitic limestone	3.5 - 16.0
Dolomitic limestone	16.0- 60.0
Slightly dolomitic limestone	60.0- 105.0
Calcitic limestone	Over 105.0

Magnesian dolomite. A pure dolomite has a ratio of 1.648 : 1 Ca/Mg but dolomites formed at elevated temperatures contain an excess of magnesite. We can place some hydrothermal dolomites in this group.

Calcareous dolomite. The selection of the upper limit here is based on the fact that the ratio of 3.44 : 1 is the lowest known in the skeletal structure of organisms. Many dolomites fall in this group and might have resulted from excess precipitation of calcium over magnesium, or may be due to incomplete dolomitization.

Highly dolomitic limestone. Several limestones composed almost entirely of skeletal parts of organisms have ratios over 16:1, even though the ratio in the skeletal parts themselves may be as low as 3.44 : 1. Diagenetic and epigenetic dolomitization may play a significant role in their origin.

Dolomitic limestones. These are mostly due to the accumulation of skeletal structures of organisms. The fine grained limestone paste may originate by direct precipitation, by comminution of skeletal structures or by diagenetic or epigenetic dolomitization.

Slightly dolomitic limestones. The upper limit of 105 selected here is due to the fact that 105.2 is the highest ratio known for calcitic organisms (oysters) and the limestone probably resulted from the accumulation of organisms. Their finer grained limestone paste is often of chemical origin.

Calcitic limestones. These may have their origin in the accumulation of aragonitic skeletal structures, by direct precipitation or from subsequent loss of magnesite. The high ratio is probably due to the low magnesium content of the cementing limestone paste precipitated from sea water.

Chemical Analysis

The results of the chemical analyses herein could not be adequately compared with those of Hamil (1961) inasmuch as his work was based on the Black River section while this was entirely Trenton. However the range of magnesium content in the two investigations was comparable.

Throughout the Trenton section dealt with in this investigation, the magnesium/calcium ratio varies from about 0.02 to a maximum of about 0.22— with the majority being about 0.05 (table 2). Inasmuch as most of the ratios fall within 0.035 and 0.075, it may be arbitrarily assumed that this represents the end points for stratigraphic dolomite. On the other hand those regions in which the ratio is significantly above or below these end points may represent epigenetic dolomite. It cannot be over-emphasized that these end points are arbitrary and are subject to change in the light of future results. It is interesting to note that some of the regions with high ratios do, in fact, have positive evidence for post-lithification dolomite. For example at 3807'-3809' and about 3785' there are fractures which have been filled by dolomite and calcite.

An attempt has been made to correlate this ratio with the radioactive logs (Fig.5). Apart from a few places where high magnesium/calcium ratios correspond with negative kicks on the neutron log and vice versa, no correlation was apparent. The apparent correspondence may be only fortuitous and so no significant reliance should be placed on it. However it is important to note the difficulty of comparing a bar graph with a smooth curve. The writer did not think a smooth curve would adequately represent the ratio or the insoluble residues,because such a curve would place the peak at a point rather than over the whole interval, and hence the picture would be very misleading.

On the whole there was a greater correlation between the results of the insoluble residue and the calcium and magnesium analyses.Most of the high and low points of the two agree although not in direct proportions. Most students of dolomitization agree that there is a significant association of dolomite and shaly partings and so one would expect a good correlation between the two in a chemical analysis. The lack of a perfect correlation (Fig.5) may be attributed to three major reasons:

1. Inasmuch as the whole Trenton section is dominantly calcitic, high calcium content necessarily means low insoluble residue and vice versa, especially since the absolute magnesium content was generally less than 10% and would average about 3.14% (Table 2).Hence the magnesium content could not exert any significant control on the amount of insoluble residue.

2. The insoluble residues are made up not only of carbonaceous, shaly materials which are known to be richer in dolomite (Carozzi,1960) but also include other siliceous materials especially cherty bands and lenses.

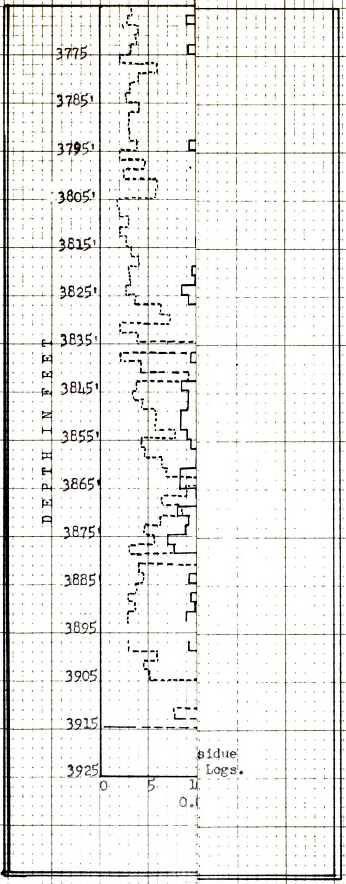
Table 2. Results of Chemical Analyses

Sample No. Depth	Calcium Oxide %	Magnesium Oxide %	Insoluble Residue %	Calcium/Magnesium Ratio.
1. 3765-67	51.68	2.959	2.3	17.47
2. 3767-69	51.70	2.70	2.0	22.78
3. 3769-71	47.54	2.862	2.9	16.62
4. 3771-73	50.54	2.917	2.8	17.33
5. 3773-75	50.13	2.371	2.2	21.13
6. 3775-77	45.69	3.756	1.1	12.16
7. 3777-79	47.08	2.568	5.0	18.38
8. 3779-81	48.72	2.865	3.0	17.00
9. 3781-83	44.39	9.788	3.2	4.62
10.3783-85	50.87	3.945	1.8	12.89
11.3785-87	49.66	5.228	3.0	9.50
12.3787-89	43.86	3.65	2.0	12.01
13.3789-91	48.87	3.698	2.0	13.21
14.3791-93	52.83	3.333	2.2	15.81
15.3793-95	49.07	2.320	2.7	21.14
16 3795-97	52.78	4.635	1.2	13.07
17.3797-99	46.92	5.285	3.6	8.88
18.3799-3801	50.99	3.828	1.5	16.76
19.3801-03	50.24	4.132	5.0	12.15
20.3803-05	54.01	4.132	4.8	13.07
21.3805-07	50.30	4.33	0.7	11.61
22.3807-09	45.70	3.529	1.0	12.95
23.3809-11	53.46	3.149	2.0	16.97
24.3811-13	49.49	6.198	1.2	7.98
25.3813-15	49.67	2.617	1.7	18.94
26.3815-17	43.97	3.120	2.3	17.34
27.3817-19	79.68	6.017	3.0	13.24
28.3819-21	88.04	3.193	2.0	25.21
29.3821-23	49.38	2.815	2.3	17.54
30.3823-25	45.95	1.788	1.7	24.69
31.3825-27	50.72	2.426	2.6	20.90
32.3827-29	46.22	2.752	5.3	16.80
33.3829-31	46.40	3.106	5.6	14.60
34.3931-33	47.30	2.957	1.2	16.0
35.3834-35	44.62	2.936	2.9	15.19
36.3835-37	47.17	2.661	9.3	17.73
37.3837-39	46.14	2.294	1.3	20.11
38.3839-41	44.92	3.716	3.3	12.09
39.3841-43	45.37	2.614	8.0	17.35
40.3843-45	47.17	1.835	2.7	25.68
41.3845-47	51.47	2.202	2.0	21.42
42.3847-49	49.33	2.361	3.0	21.80
43.3849-51	47.23	1.927	4.8	25.61
44.3851-53	47.23	1.835	4.8	25.73
45.3853-55	41.43	1.927	6.8	21.51
46.3855-57	47.37	2.431	3.5	19.48
47.3857-59	49.37	1.697	3.7	18.09
48.3859-61	49.71	2.730	5.5	18.21

Magnesium/Calcium Ratio Calculated	Corrected	Classification (After G.V. Chilingar 1957)
0.05724	0.0512	Dolomitic limestone
0.04387	0.0390	Dolomitic limestone
0.06016	0.0540	Dolomitic limestone
0.05771	0.0515	Dolomitic limestone
0.04733	0.0418	Dolomitic limestone
0.08224	0.0764	Highly dolomitic limestone
0.05441	0.0490	Dolomitic limestone
0.05882	0.0530	Dolomitic limestone
0.22610	0.2170	Highly dolomitic limestone
0.07757	0.0718	Highly dolomitic limestone
0.1053	0.0990	Highly dolomitic limestone
0.08322	0.0770	Highly dolomitic limestone
0.07568	0.0692	Highly dolomitic limestone
0.06300	0.0570	Highly dolomitic limestone
0.04729	0.0418	Dolomitic limestone
0.07649	0.0705	Highly dolomitic limestone
0.1127	0.1065	Highly dolomitic limestone
0.05967	0.0540	Dolomitic limestone
0.08224	0.0764	Highly dolomitic limestone
0.07650	0.0705	Highly dolomitic limestone
0.08592	0.0800	Highly dolomitic limestone
0.07721	0.0713	Highly dolomitic limestone
0.05892	0.0530	Highly dolomitic limestone
0.1252	0.1185	Highly dolomitic limestone
0.05279	0.0465	Dolomitic limestone
0.05768	0.0520	Dolomitic limestone
0.07553	0.0695	Highly dolomitic limestone
0.05133	0.0453	Dolomitic limestone
0.05527	0.0493	Dolomitic limestone
0.04051	0.0345	Dolomitic limestone
0.04785	0.0419	Dolomitic limestone
0.05926	0.0509	Dolomitic limestone
0.06848	0.0627	Highly dolomitic limestone
0.06250	0.0569	Highly dolomitic limestone
0.06581	0.0600	Highly dolomitic limestone
0.5638	0.0505	Dolomitic limestone
0.04973	0.0436	Dolomitic limestone
0.08271	0.0770	Highly dolomitic limestone
0.05761	0.0514	Highly dolomitic limestone
0.03894	0.0339	Dolomitic limestone
0.04669	0.0405	Dolomitic limestone
0.04586	0.0400	Dolomitic limestone
0.03904	0.0340	Dolomitic limestone
0.03887	0.0339	Dolomitic limestone
0.04649	0.0405	Dolomitic limestone
0.05134	0.0450	Dolomitic limestone
0.05529	0.0493	Dolomitic limestone
0.05491	0.049	Dolomitic limestone

Sample No.	Depth	Calcium Oxide %	Magnesium Oxide %	Insoluble Residue %	Calcium/Magnesium Ratio
49.	3861-63	44.48	1.697	5.9	26.19
50.	3863-65	42.70	1.661	10.0	25.40
51.	3865-67	50.00	2.755	8.0	18.16
52.	3867-69	49.15	4.182	5.5	11.75
53.	3869-71	46.24	1.63	7.1	28.36
54.	3871-73	52.49	2.509	5.3	20.92
55.	3873-75	53.04	2.313	3.6	22.93
56.	3875-77	48.37	1.422	4.6	34.03
57.	3877-79	51.13	1.763	2.2	31.08
58.	3879-81	43.37	2.963	11.0	14.64
59.	3881-83	51.68	3.493	3 1	14.78
60.	3883-85	50.82	2.479	3.4	20.50
61.	3885-87	51 26	2.657	2.7	19.31
62.	3887-89	53.25	2.657	2.1	20.04
63.	3889-91	47.33	2.568	2.6	18.43
64.	3891-93	52.94	2.529	1.9	20.94
65.	3893-95		No	Sample	
66.	3895-97		No	Sample	
67.	3897-99	52.90	2.60	2.1	20.34
68.	3899-3901	50.37	3.099	5.0	16.38
69.	3901-03	44.20	4.940	3.7	8.962
70.	3903-05	46.30	4.803	4.2	9.640
71.	3905-07	42.95	4.347	10.7	9.88
72.	3907-09	46.50	4.034	10.5	11.53
73.	3909-11	39.85	2.936	9.8	13.57
74.	3911-13	46.40	3.106	6.8	14.95
75.	3913-15	36.82	2.174	19.5	16.93

Magnesium/Calcium Ratio Calculated	Corrected	Classification (After G.V. Chilingar)
0.03819	0.0332	Dolomitic limestone
0.03938	0.0343	Dolomitic limestone
0.05507	0.0491	Dolomitic limestone
0.08511	0.0793	Highly dolomitic limestone
0.03526	0.0308	Dolomitic limestone
0.04780	0.0420	Dolomitic limestone
0.04361	0.0380	Dolomitic limestone
0.02939	0.019	Dolomitic limestone
0.03218	0.027	Dolomitic limestone
006829	0.0629	Highly dolomitic limestone
0.06770	0.0618	Highly dolomitic limestone
0.04877	0.0436	Dolomitic limestone
0.05178	0.0463	Dolomitic limestone
0.04987	0.0449	Dolomitic limestone
0.05426	0.0480	Dolomitic lmiestone
0.04776	0.0419	Dolomitic lmiestone
		No Sample
		No Sample
0.04915	0.043	Dolomitic limestone
0.06103	0.0552	Dolomitic limestone
0.1116	0.1051	Highly dolomitic limestone
0.1037	0.0975	Highly dolomitic limestone
0.1037	0.0971	Highly dolomitic limestone
0.08674	0.0809	Highly dolomitic limestone
0.07370	0.0676	Highly dolomitic limestone
0.06689	0.0609	Highly dolomitic limestone
0.05906	0.0538	Dolomitic limestone


DEPTH IN FEET
3775
3785'
3795'
3805'
3815'
3825'
3835'
3845'
3855'
3865'
3875'
3885'
3895
3905
3915
3925
0
5
sidue
Logs.

These cherty bodies were generally devoid of dolomite and hence would mean lower Mg/Ca and a higher percentage of insoluble residue in the section where they abound (see columnar section pp.30-47).

3. In order to make calculations easy and make results as comparable as possible with the chemical analyses for calcium and magnesium, only one gram of the prepared sample was used to determine the amount of insoluble materials. This required extreme precaution to prevent any loss of part of the sample. Unfortunately weighing the residues could be done only to two decimal places of a gram, and since a residue of 2% means 0.02 gram actual weight, each recorded figure (Table 2) should be regarded as ± 1%; but this would make only a slight change in the general picture of the graph.

Dolomitization

The application of staining techniques permitted certain observations concerning dolomitization. Although there were variations in the nature of dolomitization throughout the section, five principal types were the most abundant:

1. Abundant dolomite crystals in shaly partings.

2. Irregular spotty or patchy distribution in limestone,being richer in calcarenites and calcilutites.

3. Irregular bodies of dolomite resulting fom the dolomitization of the groundmass while the larger crystals were left unreplaced or partially replaced.

4.Partial replacement of fossil fragments, nodules, pisolites and concretions.

5. Insignificant spots in recemented fractures and chert bands and lenses.

In most cases replacement of calcite rhombs was complete and there was abundant evidence of recrystallization. However two types of incomplete replacement were noticed throughout the section. In one case each rhomb was made up of a nucleus of pure calcite rimmed by a layer of dolomitic calcite and finally a third layer of dolomite. In the second type the arrangement is reversed. It could be concluded from this type of arrangement that in the first case dolomitization progressed into the original calcite crystal and that the presence of a nucleus of calcite is probably due to the inhibition of dolomitization before complete replacement. The reverse would be true for the second case.

There were cases of greater concentration of dolomite at the shale-limestone contacts from where it spread out into the shale while dying out into the limestone. There were cases of tongues of dolomite penetrating pure limestone. These tongues were invariably located in the finer grained limestone.

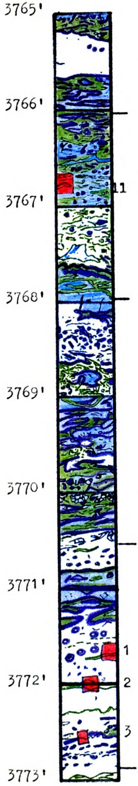
The irregular bodies of dolomite referred to above (3) were observed to be mostly due to differential replacement of the micritic groundmass, while the coarse grained crystals remained relatively unaltered. There were cases of dolomite transecting primary structures. Association with stylolitic surfaces is strongly indicative of post-consolidation origin of some of the dolomite.

Megascopic description:

The following is a megascopic description of the stained surface. Initial description was done at one foot intervals but this was later rewritten so that similar sections could be described together and so avoid repetition.

All descriptive terms used herein retain their conventional connotations. The same is true of the colors used on the columnar section, where limestone is represented by blue, purple for dolomite and green for shale.

Columnar Section of Wooden Well No.6, 3765 to 3915 feet depth.

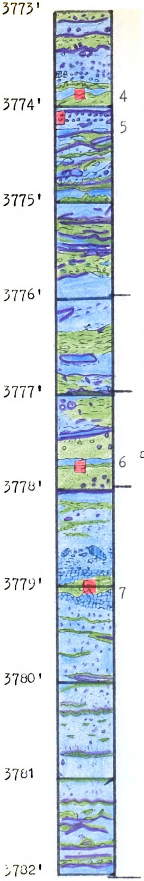


Limestone, light brown, arenaceous, banded. Top band uniformly speckled with dolomite, nodular, and bears coarse-grained calcite crystals. Bottom band shaly and dolomitic.

Limestone, brown, **shaly**, fossiliferous, **especially brachiopods, bryozoans, corals and algae**.;argillaceous and almost uniformly dolomitized. Dolomitization is in form of uniformly speckled and patchy forms, with occasional concentration around **concretions**, pisolites and fossils, and stringers parallel to shale partings. Shale partings bear rudaceous crystals of calcite, with the calcarenite progressively getting finer towards shale partings. Two vertical and one horizontal recemented fractures occur- the vertical ones being partially dolomitized.

Limestone, brown, banded and fossiliferous. Top band of arenaceous calcirudite bearing euhedral crystals of calcite, bioclastic, allochemical. Thin **stringers** and partings of shale with tongues and lenses of coarse-grained limestone with a micritic matrix largely replaced by dolomite. The underlying 18" is composed of alternating bands of limestone; with arms of calcareous shale stringers and bands; calcareous shale with tongues and lenses of limestone; and a limestone-shale layer. Texture of limestone and dolomite is semi-uniform lutaceous calcarenite grading into a rudaceous calcarenite lower down. Dolomitization is in irregular bands at shale-limestone contacts as well as patches. Replacement phenomenon is seen in dolomitized shells, nuclei of pisolites and crinoid stems.

Limestone, light brown, bioclastic, lutaceous above to arenaceous below, allochemical, with irregular layers of shaly partings and brachiopod shells (coquinoid). Abundant brachiopods, bryozoans and corals throughout. Dolomitization is speckled with greater concentration near shale layers. Stylolitic. Dolomite is more common on the lower parts of the stylolitic surfaces. Several calcite euhedra and occasional quartz grains are rimmed by dolomite.

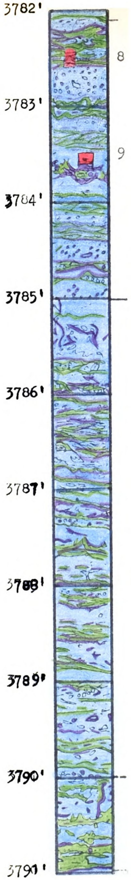


Limestone, light brown, fossiliferous, arenaceous-rudaceous, crinoidal with irregular bands of calcareous shale and argillaceous limestone bands. Dolomitization is speckled or patchy in areas but concentrated in or around the shale bands where the groundmass has been preferentially replaced, leaving scattered rudaceous crystals of euhedral or pseudohedral calcite, rimmed with dolomite.

Limestone, grayish-brown, stylolitic, arenaceous, with euhedral crystals of calcite, more fossiliferous towards the bottom. Banded with argillaceous limestone and calcareous shales, rimmed with dolomite; the lower portion being richer in dolomite than the upper. Irregular lenses of limestone rimmed with dolomite.

Limestone, light brown, siliceous, argillaceous, carbonaceous in parts with dispersed euhedral granules of calcite, crinoid stems; more dolomitic near bottom with two bands of euhedral, arenaceous-rudaceous allochemical limestone.

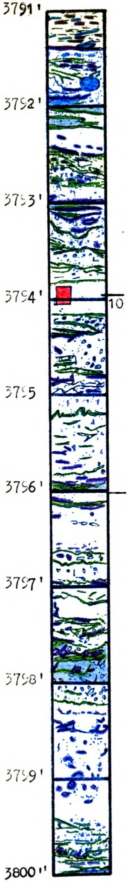
Limestone, light brown, allochemical, bioclastic, pelletal, pisolitic, with arenaceous shale bands rimmed with dolomite and with coquinoid bands. Dolomitization is patchy, speckled or associated with the shale bands and is more concentrated near the lower bands and encloses arenaceous crystals of calcite.



Limestone, grayish-brown, allochemical, bioclastic pisolitic, stylolitic, commonly fractured. Micritic limestone common in and around shale layers with occasional granules of calcite. Limestone is coarse-grained outside these layers, with the coase grains being made up of pellets, pisolites, oolites and euhedral calcite rhombs in a matrix of carbonaceous mud. This coarse-grained limestone commonly bears recemented fractures-nowhere dolomitized. Dolomitization is commonly patchy or speckled in the arenaceous limestone or as rims of shale partings where they tend to fan out into the finer-grained limestone. They also show a vein type effect at limestone-shale contacts, and coarse-grained and finer-grained limestone contacts. Limestone nodules and pellets are enclosed in dolomite in places. There is a tendency towards preferential replacement of the groundmass of limestone by dolomite, leaving rudaceous-arenaceous crystals of calcite. Veinlets of calcite cut into, but not across concretionary features.

Limestone, light brown, arenaceous, rudaceous in parts pisolitic, nodular, carbonaceous in parts, fossiliferous, with bands of calcareous shale and argillaceous limestone enclosing lenses, tongues and other irregular bodies of arenaceous limestone. The shales bear dispersed crystals of calcite. Dolomitization is speckled and patchy throughout the section; with greater concentration around shaly bodies and arenaceous-rudaceous crystals of calcite, pisolites, nodules and concretions, because these are set in a matrix of micrite. Interior of most shales are dolomite poor. Speckled dolomites enclose 'ghosts' of calcite. A Y-shaped fracture has dolomite spots in the cement; and cuts across stylolitic boundaries and clay partings-evidently post-consolidation. From 3789-90' the limestone is more coarsely crystalline, less dolomitic and has thinner shale partings.

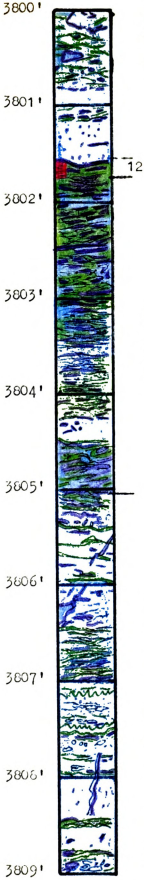
Limestone, light brown, rudaceous-arenaceous, nodular, banded with irregular bodies of carbonaceous and calcareous shale. The six major bands of limestone are coarse-grained, predominantly a calcarenite, often ranging to calcirudite in places. About 3791.7 there is a limestone concretion about 2" in diameter. Banding



is very distinct near the bottom. The shale bands host euhedral calcite crystals. A shale band, about 6" wide, at 3791' is made up of several stringers and veinlets in a patchy background of calcilutite, and occasional rudaceous crystals, pisolites and nodules. Dolomitization is predominant near some shale bands, elsewhere it is patchy, spotty or occurs as stringers at limestone-shale contacts. Dolomite is lacking in the calcarenite, but is more concentrated in the limestone tongues interspersed in the shale layers.

Limestone, brown, oolitic, pisolitic, bioclastic, nodular, with variously oriented calcite rhombs. Texture varies progressively from lutaceos-arenaceous on top to rudaceous at the bottom. There are numerous stringers of calcareous shale and carbonaceous shale partings with numerous calcite rhombs scattered all through. Dolomitization presents a speckled and powdery appearance with no preferential concentration around shale bodies, except in some micritic limestone. Replacement features are seen in 'ghosts' of calcite in dolomite rhombs; and both intra-crystal and extra-crystal origins are indicated.

Limestone, brown, allochemical, pisolitic, banded, fossiliferous, stylolitic, the top 3' is predominantly arenaceous while the lower portion is made up of arenaceous crystals of calcite in a micritic groundmass; partially silicified towards the bottom. Shale stringers, bands and partings are insignificant at the upper part but very strong at 3799.5-3800.6'. This zone is almost uniformly argillaceous with lutaceous limestone lenses and tongues, fossils, pisolites, nodules and pellets scattered throughout . Dolomitization is mottled and patchy in places and presents strong evidence for late stage replacement. Some pure calcite crystals are rimmed by dolomite and then by calcite. Fossil shells, although not replaced, are filled with calcite, some of which have been replaced by dolomite. There is no



significant concentration of dolomite anywhere except around some fossils, pisolites and nodules. There appears to be a preferential dolomitization of the groundmass of coarse-grained calcite in the shale areas.

Limestone, brown, strongly argillaceous, fossiliferous nodular, and dolomitic. It is so greatly argillaceous as to appear as a uniform shale band. The argillaceous limestone bodies enclose lenees and tongues of arenaceous limestone. Most significant dolomitization consists of stringers, lenses and tongues , mostly composed of euhedral rhombs enclosing calcite.

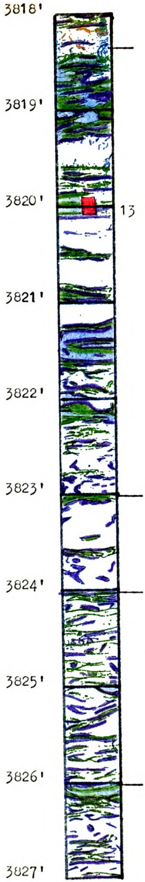
Limestone, light brown, fossiliferous, pisolitic, nodular, allochemical, argillaceous and micritic in places. The top is chiefly coralline while the lower portions are richer in brachiopods and bryozoans. The limestone varies from an aphanitic band on top, to arenaceous-rudaceous lower down, with euhedral calcite crystals. Local and preferential silicification has led to chert blebs and silicified brachiopod shells. Calcareous shale partings very few and stylolitic. Dolomitization occurs both in shales and as irregular bodies in the interstices of coarse-grained calcite crystals, it is patchy and speckled all through, and as stringers in fossiliferous layers. A number of brachiopod shells are filled with calcite and dolomite rhombs some of which have 'ghosts' of calcite. Vertical fractures are common and all these are filled with calcite and dolomite. Stylolites are common in this section but in no case is dolomite associated with them.

3809'
3810'
3811'
3812'
3813'
3814'
3815'
3816'

Limestone, brown, rudaceous to arenaceous, occurring as lenses, tongues and sausage-shaped bodies surrounded by argillaceous bodies. Carbonaceous shale bodies of irregular geometry are dominant and enclose nodules, crinoids and a few other fossils, and have rudaceous calcite crystals scattered through them. Dolomitization is as above.

Limestone, nodular, stylolitic, arenaceous, allochemical, argillaceous with shale bands, most of which have stylolitic contacts with limestone. Dolomitization is as above but stronger towards the top.

Limestone, brown, crinoidal, pisolitic, argillaceous fossiliferous, arenaceous-rudaceous , and banded. The lower section is more fossiliferous while the top is mostly allochemical and stylolitic. The calcareous-carbonaceous shale bodies occur as stringers, partings, and bands with tongues and lenses of arenaceous limestone whose groundmass consist of lutaceous-arenaceous dolomite rhombs. Dolomitization in the shale-limestone contacts is almost uniform except for spots which represent coarse-grained calcite crystals that have not been replaced .Elsewhere dolomite



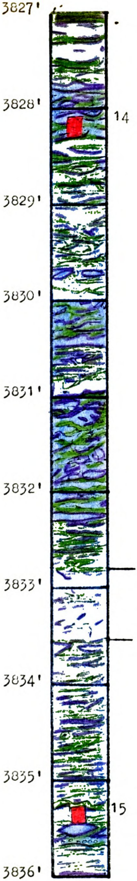
occurs as patches , spots and irregular bodies in limestone.

Limestone, light brown, banded, fossiliferous, rudaceous with euhedral calcite crystals. Alternating sub-equal bands of limestone and calcareous shale. The limestone bands lower down are more fossiliferous nodular and pelletal. The calcareous- carbonaceous shale bands are of irregular shape and enclose lenses and stringers of limestone which are invariably arenaceous-rudaceous and also have euhedral calcite crystals scattered through them. The shale bands are fossiliferous especially near the bottom of the section. Predominant dolomitization is confined to the shale-limestone contacts from where it fans out into the shale.Other modes of occurrence are as rims of nodules, fossils and rudaceous calcite crystals. The limestone bands in the middle section are poor in dolomite but the others are speckled with it.

Limestone, brown, allochemical, nodular; bryozoan--bearing, pisolitic,arenaceous calcirudite with two thin bands of shale . Patchy dolomitization.

Limestone, light brown, lutaceous-arenaceous, lenticular-sausage-shaped. Irregular stringers of calcareous shale enclose lenses of boudin-like limestone bodies which are arenaceous generally. Dolomitization spotty.

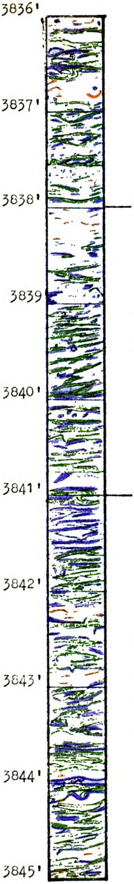
Limestone, generally as above but more arenaceous-



rudaceous , with more nodules, fossils, pisolites and pellets. The limestone and shale show a better banded appearance and dolomitization is in form of stringers at contacts of the bands and also as rims of nodules, fossils and calcite rhombs. Obviously a replacement feature. Local silicification seen in chert needles and silicified shells.

Limestone, light brown, banded, arenaceous, **cherty** and interbedded with calcareous shale and shale. Dolomitization is almost regular in the shaly bands, spotty in limestone.

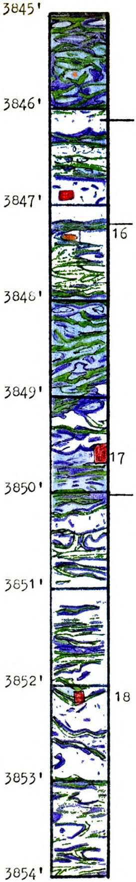
Limestone, grayish-brown, arenaceous, nodular, pelletal and partially silicified. The shale bands are as in other parts and enclose limestone bodies of various outlines. Silicification is partial and tends to be restricted to brachiopod shells most of which are convex upwards. Dolomitization is poor towards the bottom where it is speckled, but elsewhere it appears as a powdery coating of shales and also as stringers at the limestone -shale contacts where they fan out into the shale .Irregular patches of



dolomite occur in places enclosing euhedral rudaceous calcite crystals while the finer groundmass of dolomite enclose nuclei of unreplaced calcite crystals.

Limestone, light brown, uniformly arenaceous with scattered nodules , crinoid stems, brachiopod shells, chert lenses and irregular and discontinuous shale bodies enclosing lenticular and sausage-shaped limestone bodies. Dolomitization is patchy or speckled . Limestone is rudaceous towards the bottom.

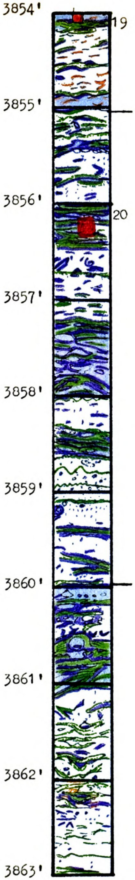
Limestone,light brown , consisting of alternating bands and lenses of rudaceous and lutaceous calcarenite and calcirudite, interbanded with calcareous shale bands and stringers. Fossiliferous, cherty and nodular. Dolomitization is in form of irregular stringers in shale as well as rims of shales. It occurs as patches and spots in other places , while it has an irregular outline where it has replaced the micritic groundmass of arenaceous-rudaceous limestone lenses and tongues. Calcite'ghosts' are common in dolomite areas.



Limestone, dark brown, irregularly banded, arenaceous nodular with thin irregular bands of shale. Dolomitization is mottled or patchy and is more dominant in the micritic groundmass.

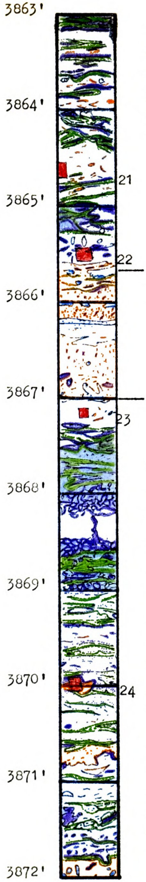
Limestone, grayish-brown, arenaceous-rudaceous, fossiliferous, (chiefly brachiopods and ostracods), cherty, stylolitic with shale bodies of irregular shape and outline which are mostly fossiliferous especially around 3849.5' where a planispiral gastropod shell bears some dots of dolomite . The chert lenses are oriented parallel to bedding. Dolomitization is most prominent around 3848.8' but occurs as stringers elsewhere in shale regions and as patches, spots and other irregular bodies in limestone. It encloses rudaceous crystals of calcite locally. There are occasional quartz grains.

Limestone, light brown, alternating bands of arenaceous calcilutite and rudaceous calcarenite, fossiliferous, pisolitic-oolitic, nodular, cherty and with occasional quartz grains. The shale bodies vary in shape and outline, but occur mainly as bands , stringers and partings with stylolitic boundaries with limestone; while at the same time enclosing variously shaped bodies of limestone invariably of coarser crystals than those outside the shale. Dolomitization is as above but also occurs as dots in chert lenses, and hence younger than silicification. Preferential replacement of nodules and fossil shells are common and occur at limestone-shale contacts , at the same time presenting a powdery appearance in shale.



Limestone, grayish brown, cherty, pelletal, stylolitic fossiliferous, pisolitic , arenaceous-rudaceous with irregular stringers and bands of calcareous shale enclosing limestone lenses and tongues. Some fossil shells are concentrated at the limestone-shale contacts giving a coquinoid appearance ,while others form thin layers in limestone. The randomly scattered shells have been mostly silicified. Most of the chert lenses are oriented parallel to bedding . Dolomitization is more prevalent in the shale section where it occurs as stringers and laminae of variable geometry. In the limestone areas it occurs as patches, spots and other irregular bodies. A fracture occurs around 3856.3' which is associated with two chert lenses, and has been filled with calcite and dolomite rhombs.

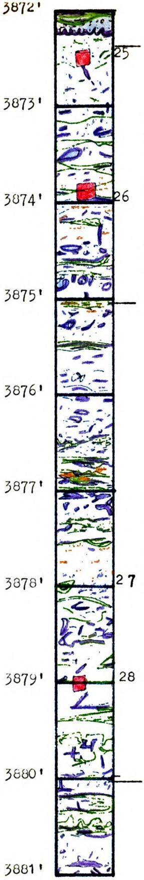
Limestone, grayish-brown, banded, lenticular, argillaceous, fossiliferous, cherty, stylolitic, pisolitic-oolitic and lutaceous calcarenite, with thin bands ,stringers and threads of shale. The chert lenses are very abundant especially at 3861-62' and the bottom 2'. Most of these chert lenses are replacements of brachiopod shells oriented parallel to bedding. The irregular shale bodies enclose limestone lenses and tongues and also have euhedral calcite crystals scattered through them. Fossil shells are especially



abundant at the limestone-shale contacts. Dolomitization is generally mottled or patchy except in shales where it forms rims and then fans out into them, while dying out into the limestone. Some of the chert lenses have spots of dolomite and hence younger than chert. Replacements of nuclei of pisolites, oolites and fillings of silicified shells are very common.

Calcareous chert, grayish brown, made up of two bands on either side of an arenaceous limestone band about $2\frac{1}{2}$" thick. Dolomitization spotty.

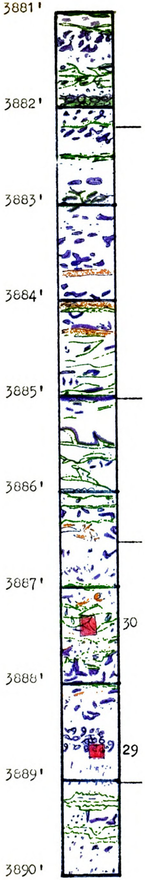
Alternating bands of shales and limestone. The limestone bands are arenaceous-rudaceous, fossiliferous, stylolitic and carbonaceous towards the top. Bands at 3868' consist of two fossiliferous calcirudite bands and one of calcarenite between them. In other places the relation is not so well defined- all bands being rudaceous calcarenites. Two geodes at 3871.5'. Fossils are abundant all over the section- especially brachiopods, ostracods, bryozoans and corals. However, they form some coquinoid layers in limestone and shales. Some of these shells are replaced by chert. Chert lenses are numerous and they are oriented parallel to bedding. Two calcareous chert bands and a tongue occur in the lower half of the section. The shale bodies are of irregular geometry- the thicker ones being made up of numerous stringers, They enclose several lenses and tongues of limestone,and commonly have stylolitic boundaries with limestone. Dolomitization is conspicuously spotty, with local concentration in shales, around nodules, fossils, limestone lenses and tongues, and as fillings of some fossils. The uniformly coarse-grained limestones (calcarenites and calcirudites) are conspicuously lacking in dolomite, while those which have diversified textures (lutaceous calcarenites,etc) tend to have their matrix replaced and recrystallized. Incomplete replacement of calcite by dolomite shows evidence for both inward and outward growth of dolomite.



Limestone, light brown, fossiliferous, siliceous, cherty, stylolitic, arenaceous-rudaceous calcilutite; with occasional bands of calcarenite. There are fewer fossils than above, mainly brachiopods and bryozoans, and they have been mostly silicified. Shale bodies are irregular but stringers are more common. One chert band at 3886'. Dolomitization is speckled, patchy and irregular. Argillaceous limestones are rich in dolomite. Siliceous limestones on the other hand are dolomitic only where they are bounded by shale partings. Some shale bodies enclose pockets of dolomite.

Limestone, light brown, banded, stylolitic, locally silicified, only slightly fossiliferous, locally carbonaceous, arenaceous to rudaceous. Locally lutaceous. Shale stringers and bands are carbonaceous and have a coarsely arenaceous background. Silicification is in form of chert lenses, bands and tongues of calcareous chert. Dolomitization is patchy as well as dots in fracture fillings and chert bands.

Limestone, brown, rudaceous at top becoming lutaceous

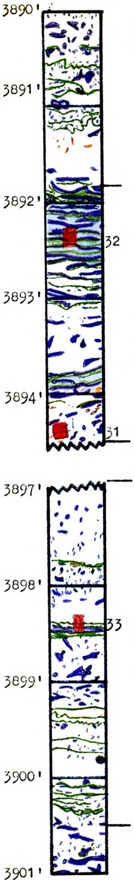


lower down; fractured,locally carbonaceous, fossiliferous, with thicker carbonaceous shale bands.Locally silicified with patchy dolomitization.

Limestone, light brown, locally siliceous, increasingly fossiliferous towards the bottom, stylolitic, arenaceous with two chert bands and a few shale stringers. Dolomitization occurs as patches and occasional lenticular bodies with sharp tongues penetrating the arenaceous limestone.Scattered quartz grains.

Limestone, grayish brown, medium grained calcarenite, argillaceous, siliceous, fossiliferous, coquinoid in parts with silicified geodes. A band of brachiopod shells and some corals and bryozoans occurs at 3882.2'. Stringers and threads of shales spotted with dolomite. Entire limestone section bears patches of dolomite.

Limestone, light brown, fossiliferous, cherty,rudace-



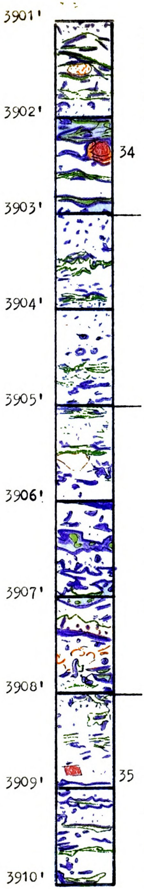
ous arenaceous, stylolitic with shale stringers and irregular patches, stringers and speckles of dolomite.

Limestone, brown, fossiliferous, arenaceous-rudaceous, with local bands of micrite; stylolitic, banded with irregular bodies of dolomitic shale. Dolomite patches elsewhere. Silicified fossils near bottom and some silicified patches have some dolomite spots.

3894.5
No Core
3897'

Limestone, grayish brown, finely arenaceous, stylolitic, banded, cherty, micritic in places, fossiliferous with irregular stringers and bands of shale locally speckled with dolomite. Dolomite occurs as coarsely arenaceous patches in limestone and fillings of fossils.

Limestone, grayish brown, finely-moderately arenace-



ous, micritic in parts, with occasional coarsely arenaceous patches and lenses, stylolitic, cherty, with stringers and partings of calcareous shale. Two lenses of calcareous chert. Dolomite occurs as rims of shale as well as patches and specks in limestone - with pronounced evidence for replacement and recrystallization.

Limestone, moderately arenaceous, with irregular bands of shale, silicified fossils, and patchy, mottled dolomitization. Nodules and pisolites partially replaced or transected by dolomite.

Limestone, light brown, finely arenaceous-lutaceous, semi-lithographic in parts, siliceous - generally an arenaceous calcilutite. Chert concretion at top, a band towards the bottom and lenses of silicified fossils. The chert band has a stylolitic upper contact with limestone and a vertical fracture which has been filled with dolomite and calcite. Dolomitization is dominantly patchy but also occurs as rims of shale.

Limestone, grayish brown, fossiliferous —generally an arenaceous calcilutite. Stylolitic, pelletal, carbonaceous, semi-lithographic, pisolitic in parts, argillaceous , ferruginous locally, nodular and siliceous with irregular bands of dolomitic shale. Dolomitization occurs as recrystallized patches in limestone,

3910'

3911'

3912'

3913'

3914'

3915

as well as rims of limestone lenses and shale bands.

Limestone, grayish brown, pelletal, siliceous, nodular, argillaceous, cherty towards the bottom, semi-lithographic locally but generally an arenaceous calcilutite; calcareous shale stringers enclose chert or limestone lenses and tongues, and are rimmed with dolomite. Cherty bands prominent near the bottom and are obviously pre-dolomitization, since fractures both in and outside the chert bands are partially filled with dolomite. Nodules and fossils are silicified. Dolomitization patchy and speckled.

No core.

Legend

Chert

Dolomite

Limestone

Shale

Locations of Thin Sections

[illegible]

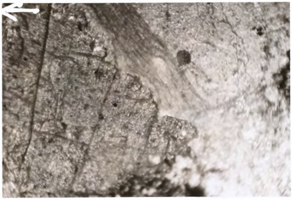
Microscopic Description

Unlike Kirschke (1961) who selected samples for thin sectioning at two feet intervals, the writer attempted to select his samples in such a way that all lithologic variations were represented.

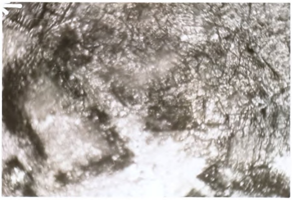
Inasmuch as the nature of dolomitization is the principal objective of this study, the writer has laid a greater emphasis on the variation in texture and structure of dolomitized areas of the thin sections. The description accompanying each photograph represents the observation made on the whole slide and not just the area covered by the photograph.

The writer has strictly adhered to conventional connotations of descriptive terms. For example arenaceous and lutaceous retain their textural implications. Except in two cases (see photographs) the magnification for all the photographs is 75 times the true size.

1. 3771.7' Fossiliferous, locally pelletal, lutaceous in parts but generally a calcarenite, bearing a few patches of dolomite, and irregular stringers of carbonaceous shale.

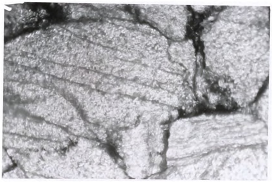


2. 3772' Calcarenite with some interlocking coarse calcite crystals are set in a matrix of argillaceous micrite. Dolomitization speckled near the top.



3. 3772.5' Finely arenaceous limestone locally lutaceous. Dolomitization is in form of incomplete replacement of calcite, most predominant in shale. Fossiliferous, stylolitic.

4. 3773.8 **Coarsely-crystalline** calcarenite with scattered quartz grains and irregular bodies of chert and opaline silica. Dolomite occurs on one side mostly as few scattered rhombs enclosing calcite. Fossiliferous and with minor shale stringers near the top. Recrystallised with moderate sorting.

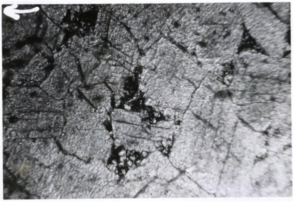


x 100

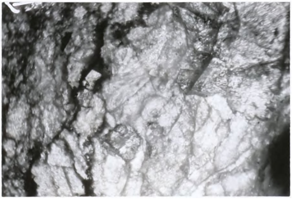
5.3774.2' Moderately fossiliferous, locally shaly rudite and calcarenite, speckled with dolomite crystals enclosing ghosts of calcite. Recrystallized.

6.3777.8' Calcarenite admixed with lutite and rudite. Locally argillaceous, sparsely dolomitized. Fossiliferous.

7.3779' Interlocking coarsely-arenaceous crystals of calcite held together by a maze of carbonaceous shale stringers near the top. Elsewhere shale is insignificant.Scattered rhombs of dolomite and quartz grains. Small tongues of crypto-crystalline silica— mostly chert.

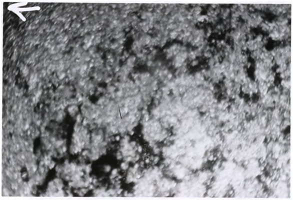


8.3782.5' Arenaceous limestone, fossiliferous. Calcite crystals are mostly pseudohedral .Dolomite occurs as incomplete replacement of calcite rhombs and is most abundant in shaly regions. Outside the shale region and towards the bottom, the limestone is arenaceous and is entirely dolomite free.

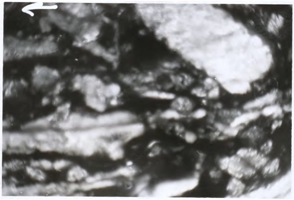


9.3783.7' Fossiliferous, argillaceous calcarenite and some rudite, highly dolomitic towards the bottom. The limestone becomes lutaceous near the bottom and is speckled with dolomite, most of which occurs as an interlocking mosaic of coarsely-lutaceous rhombs enclosing calcite rhombs or quartz grains.Pisolite partly rimmed by dolomite rhombs.

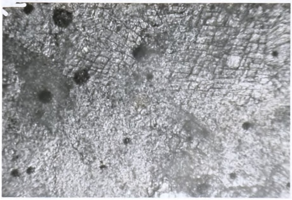
10.3794.2' Lutite and calcarenite. rudaceous towards the bottom. Locally cherty. Dolomite crystals and patches are most abundant in a band of argillaceous limestone of micritic texture.



11.3766.7' Calcarenite, locally fossiliferous and argillaceous. Dolomitization consists of several arenaceous crystals of dolomite associated with shale.

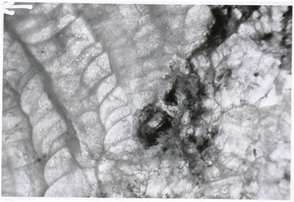


12.3801.6' Pelletal, dolomitic and strongly argillaceous limestone. Shale consists of a cluster of stringers with interlocking crystals of dolomite and some calcite.

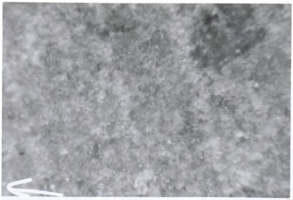


13.3820' Fossiliferous calcarenite Pelletal towards the bottom and shaly near the top with scattered euhedral calcite rhombs and quartz grains. Undolomitized.

14.3828.1' Generally a lutaceous limestone with a few stringers of micritic limestone and shale. A few scattered dolomite crystals occur near the bottom of one corner. Four lenses of chert occur in this area.

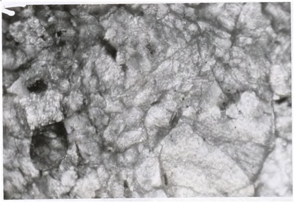


15.3835.4' Finely arenaceous limestone towards the bottom. Locally fossiliferous, cherty and pelletal with a few quartz grains. Near the top is a band of argillaceous material consisting of a network of shale stringers which enclose lenses and tongues of calcite and dolomite rhombs.One quartz grain rimmed by dolomite near the middle.

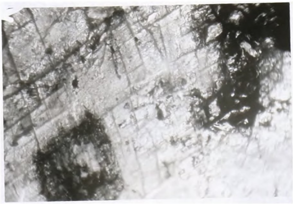


16.3847.4' Arenaceous limestone,locally fossiliferous and argillaceous. There are **three major areas — two** near the middle and the third near the bottom. They consist of an interlocking mosaic **of coarse** dolomite rhombs embedded in round bodies of argillaceous limestone mud.

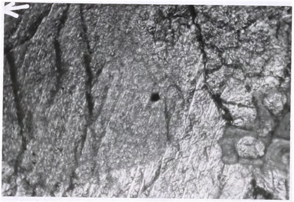
17.3849.6 Fossiliferous calcarenite, locally pisolitic.Argillaceous near the top . Largely undolomitized.



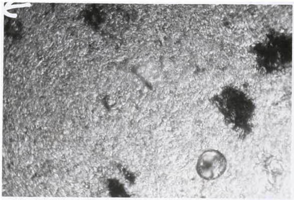
18.3852.1 Well sorted, pelletal, fossiliferous and lutaceous limestone.Largely undolomitic except for two patches of dolomite near the bottom.



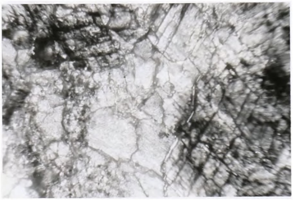
19.3854.1 Arenaceous calcite crystals in a lutaceous matrix.There are a few irregular stringers of shale and fossils; undolomitic.



20.3856.3 Lutaceous to finely arenaceous limestone,with bands of shale.The shale encloses moderately lutaceous rhombs of dolomite and finer crystals of calcite. Dolomite occurs as speckles throughout the remaining parts of the area.



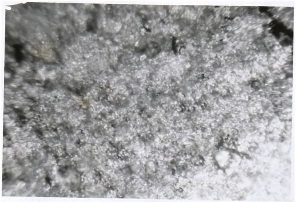
21.3864.6 Lutaceous limestone with a few arenaceous crystals of calcite and some chert lenses. Anhedral, moderately arenaceous rhombs of dolomite are scattered throughout the field. The shale bodies enclose lenticular bodies of micrite.



22.3865.5 Calcarenite with a pocket of carbonaceous shale bearing scattered calcite crystals.

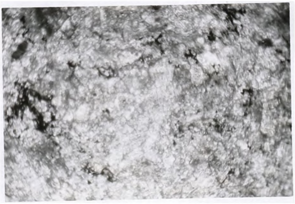
23.3867;2 Moderately well sorted calcarenite, pelletal, pisolitic and fossiliferous.

24.3856.2 Calcareous shale. The shale consists of a complex network of stringers enclosing lutaceous crystals of calcite and quartz grains; fossiliferous.

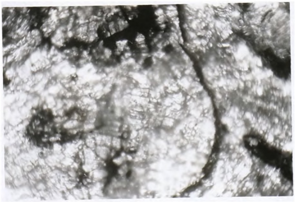


25.3872.5 Arenaceous limestone, foss-iliferous and with shale stringers enclosing calcite and dolomite rhombs. Two patches of dolomite occur near the top.

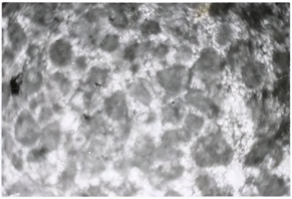
26.3873.9 Dominantly a calcilutite with local arenaceous texture. Patchy to speckled dolomitization. Irregular bodies of shale.



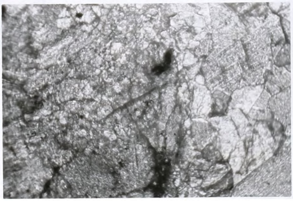
27.3878.1 Moderately well sorted calcarenite, pelletal pisolitic and fossiliferous.



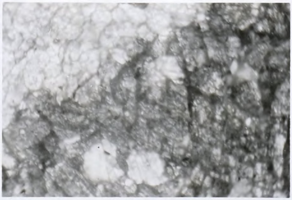
28.3879' Uniformly fine-grained limestone, essentially a calcilutite. It is stylolitic and dolomitization is spotty.



29.3888.6 Very fossiliferous, arenaceous limestone, with quartz grains scattered here and there. The arenaceous crystals are set in a groundmass of micrite. Shale consists of irregular stringers and carbonaceous patches- largely undolomitic.

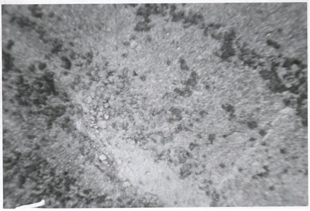


30.3887.4 Lutaceous to semilithographic limestone with dispersed crystals of arenaceous calcite; and bearing irregular patches of calcitic dolomite, with few stringers of shale. There are some fossils and fractures bearing some dolomite.

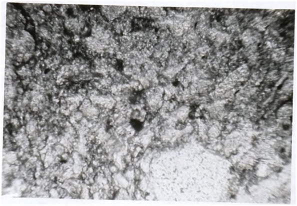


31.3894.3' Lutaceous micrite with two argillaceous bands filled with coarser-grained **dolomite** rhombs;pelletal near the bottom.

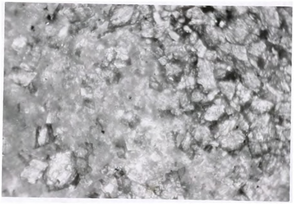
32.3892.4 Dolomitic calcilutite, locally finely arenaceous. Dolomite occurs as irregular patches. Local bands of micrite.



33.3898.4 Finely arenaceous,stylolitic and fossiliferous limestone, with bands of argillaceous calcarenite.Some of the bands bear lutaceous crystals of dolomite, but on the whole, dolomite is insignificant.

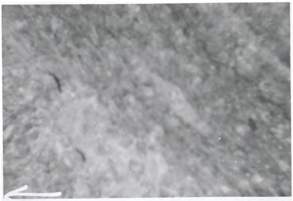


34.3902.4 Calcilutite enclosing a tongue of cherty micrite. The cherty micrite bears numerous rhombs of dolomite.Dolomite in the lutite is also speckled but it is very dense and gives an almost uniformly blue stained appearance with a definite contact with the cherty micrite.



35.3908.8 Lutaceous micrite with patches of dolomitic limestone. It bears several parallel shale stringers with calcite veinlets and is locally arenaceous at the bottom.

36.3913.1. Calcarenite, divided into parts by a band of argillaceous limestone.The argillaceous limestone consists of a maze of shale stringers enclosing anhedral,lutaceous crystals of calcite and quartz Above the shale band, the limestone is speckled with dolomite crystals which are larger than the calcite groundmass.The top is fossiliferous.



SUMMARY AND CONCLUSIONS

In one of the first parts of the problem, Kirschke (1962) suggested that'the lack of appreciable pin point or vuggy porosity would infer replacement dolomitization, possibly early diagenetic.' The writer has recorded a number of features (see columnar section) which suggest very strongly that dolomitization here is a replacement phenomenon. Most important of these are:

1. Great range in chemical composition (Table 2).
2. Dolomitization of fossils, fossil fillings and oolites.
3. Speckled nature.
4. Calcite 'ghosts' in some dolomite rhombs.
5. Nests of dolomite in limestone, mostly due to preferrential replacement of the groundmass of coarsely-crystalline limestone.
6. Irregular contacts of limestone and dolomite.
7. Pseudostratification effects.

Any direct precipitation theory would have a lot of trouble explaining these features as well as the great abundance of fossils. They are however easier to explain by invoking a replacement origin.

Hamil, (1961) on the other hand , recognized two important zones- 4232'-4258' and 4291'-4311' depth in the Peterson Howard well core, and suggested that the zones "are more likely to have a stratigraphic origin due to the consistently high magnesium content, through a large thickness. It will, of course, take similar studies of other wells to show which, if any of these zones are stratigraphic." The writer has also noted two similar zones of consistently high magnesium content — 3797'-3805' and 3899'-3913' depth. However the writer could not suggest a possible origin of the dolomite in these zones without reservation.The writer is not suggesting correlation of these zones in the two wells, as the core studied herein is of younger age (Trenton) than in Hamil's study (Black River).

In the present investigation the writer does not feel that it is possible to separate diagenetic (elsewhere referred to as ' stratigraphic') dolomite from the epigenetic dolomite. This is because the evidences which indicate each origin are not restricted to any particular depth zone, although they may be more strongly indicative of one than the other.

The following three properties were observed in the petrographic aspects of the investigation while the fourth is inferred from the results of the chemical analyses:

1. Tendency for dolomitization to follow stratification, shale partings and limestone-shale contacts.

2. Spreading of dolomite in all directions.

3. Occurrence of perfect rhombs of dolomite in incompletely altered limestone.

4. Semi-uniform chemical composition over a considerable thickness suggests that the dolomitizing agent operated over a long period of time.

All these evidences are clearly indicative of early alteration and so the dolomite may be regarded as being diagenetic. On the other hand the following additional features indicate an epigenetic origin.

1. Dolomite spots on upper surfaces of stylolites.

2. Dolomite tongues penetrating limestone beds.

3. Partial dolomitization of fossils and fossil fillings.

4. Dolomite spots in fracture fillings.

Inasmuch as there is no stratigraphic boundary between these two types of dolomite, we may assume that the magnesium content of the stratigraphic dolomite would be fairly uniform (Table 2). This is the basis of the assumption that conspicuosly low magnesium/calcium ratios probably represent areas that were not altered during the first phase of dolomitization, and hence the dolomite is epigenetic. In the same way conspicuously high figures could be attributed to an epigenetic enrichment of the earlier diagenetic dolomite. Since most of the samples have magnesium/calcium ratios falling within 0.035 and 0.075, they have been arbitrarily selected as end points for areas where the stratigraphic type is more significant than the epigenetic dolomite.

As pointed out earlier the most significant occurrence of dolomite is that associated with shale partings. Several reasons may account for this common occurrence but only four will be suggested herein.

1. Shale partings were probably the dominant channels through which magnesian solutions migrated.

2. Inasmuch as most of the shales are carbonaceous, they might have had a greater concentration of magnesium compounds than the surrounding areas. These magnesium compounds could start off the process of dolomitization even when the magnesium content in the invading solutions is not sufficient to start the same process in the adjacent limestone areas.

3. If the original clay was montmorillonite (or illite) the original magnesium content might be helpful in creating the same condition as (2).

4. The shale-dolomite association may also be related to the amount of humic acids permeating the rocks.

It is not known which of these is the most significant, but it is not impossible that they could all have been contributory.

Patchy distribution of dolomite was probably a result of selective replacement in and around the shale partings. Outside the shale partings permeability might have been the most important factor influencing replacement. Consequently dolomite patches are larger, more abundant and more clearly defined in areas where shale partings are thin or few . The reverse is in cases of thick or more numerous partings. In the first case solutions are slowed down and so increase the opportunity for replacement (Carozzi, 1960).

In the coarse-grained limestone the matrix is replaced first, and thereafter the coarser grains and fossils. This is because the finer the material the greater the surface area exposed to the dolomitizing fluids, and hence they are more susceptible.

The oolitic-pisolitic textures that were very conspicuous in the megascopic observations were not readily apparent under the microscope owing to alteration.They were represented by structureless , rounded and darker areas.

The relation between calcareous chert bands, chert lenses, and dolomite is not altogether clear. In some cases they were spots of dolomite in chert, but most of the chert bodies were devoid of it. The earlier-fórmed chert may be due to lower alkalinity in the environment (Carozzi 1960). Silica was precipitated to the exclusion of dolomite which formed at higher alkalinity . There were at least two periods of silicification and it is believed that each of these periods was earlier than the corresponding period of dolomitization (see columnar section).

The writer does not believe that future work would be able to draw a line onclusively between diagenetic and epigenetic dolomitization believed to be present in the Ordovician limestones of Michigan. Such work would only be able to locate stratigraphic horizons where diagenetic dolomite is more significant than that of epigenetic origin.

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