Dolomitization Processes in the Palaeozoic Horizons of Manitoba.

by

Donald J. Birse. B. Sc.

Presented in partial fulfillment of the requirements for the Master of Science degree in the University of Manitoba.

April 1928.

Table of Contents.

Introduction.

The material contained in this thesis is the result of an investigation made on rocks from certain Manitoba palaeozoic horizons in which dolomitization processes have been active. A note has also been added on a mottled drift boulder from Gimili, Manitoba.

Normal dolomite, $CaMg(CO_3)_2$ consists of 54.35% calcium carbonate, and the remainder, 45.65%, magnesium carbonate. Pure dolomite has rarely been found, dolomite with impurities of siliceous and argillaceous material together with iron and related minerals more commonly occuring. In a great many dolomites the percentage of calcium is far in excess of the normal amount and at times it is difficult to draw the boundary between limestone and dolomite.

This paper will refer to those rocks composed entirely of dolomite crystals as "dolomites", those with dolomite and calcite crystals as "dolomitic limestones", and those with approximately 2% of magnesium carbonate, but with no dolomite crystals developed, as "magnesian limestones."

Historical Summary: In 1779 Arduino, an Italian Geologist, called attention to the "magnesian limestones" of the Tyrol which occur associated with rocks of volcanic origin. Two years later Dolimeu described some of their properties. In 1792 de Saussure recognized the rock as being a species distinct from limestone and gave to it the specific name "dolomite", in honor of its first describer. From that time on to the time of Clifton Sorby(1879) the investigation was of a chemical geological nature. Since 1879 dolomite has been found to constitute one of the most important rocks of the earth's crust. Much has been written on the subject and certain facts have been established regarding its origin.

Dolomite has been formed by the dolomitization of limestones after emergence from the sea; such(subsequent) dolomitization having been effected by percolating ground waters carrying magnesium carbonate in solution.

Limestones have also been dolomitized before emergence from the sea; such(contemporaneous) dolomitization having taken place by secondary changes in the calcareous ooze.

The possibility of the formation of dolomite by chemical precipitation in the sea has been considered and at present there exists a wide divergence of opinion among geologists as to the importance of such a process in dolomite building.

The occurrence of clastic dolomites derivied from pre-existing rocks of a similar mature, although well known, is unimportant, as it has no bearing on the ultimate origin.

Experimental Data: Considerable experimental work has been carried out on the production of dolomite but the information obtained is of very little value in determining the conditions under which the rock has been formed in nature. All the experiments have been carried out either at high temperature or pressure, or both, but only rarely at ordinary temperature and pressure. In the last case only minute amounts of dolomite have been formed and that under conditions that doubtfully obtain in nature. Recent work by Wyckoff and Merwin[1] indicates that ferrous carbonate may be a medium through which dolomite

---

1. Wyckoff, R.W.G., and Merwin, H.G., Am. Jl. Sc. 5, Vol. 8, 1924, p. 447.

can be prepared experimentally.

Palaeozoic Stratigraphy in Manitoba: The Devonian and Silurian succession were worked out by Kindle[2] and the Ordovician by Dowling[3].

	Manitoba Limestone	185 feet.
Devonian	Winnipegosan Dolomite	168 " .
	Elm Point Limestone	25 " .
	Leperditia hisingeri zone	100 " .
Silurian	Gypsum Beds	150 " .
	Virgiana decussata zone[4]	135 " .
	Stony Mountain Shales	190 " .
	Upper Mottled Limestone	130 " .
Ordovician	Cat Head Limestone	70 " .
	Lower Mottled Limestone	70 " .
	Winnipeg Sandstone	100 " .

The Winnipeg Sandstone consists of beds of soft friable white sandstone, containing few fossils.

The Lower Mottled Limestone rests on the shaly upper beds of the Winnipeg Sandstone. Near its base the formation is argillaceous but elsewhere it is a yellowish or buff colored

---

[2] Kindle, E.M., G.S.C. Sum. Rept. 1912.

[3] Dowling, D.B., G.S.C. Ann. Rept., 1900.

[4] Savage, T.E., and Van Tuyl, F.M., Bull. G.S.A., Vol. 30, 1919, p. 339.

limestone characterized by dark brown spots which give to the rock a mottled appearance. The formation contains many fossils.

The Cat Head Limestone is more dolomitic than the Upper and Lower mottled formations that lie above and below it respectively. In no place has the rock a mottled appearance. The formation is highly fossiliferous.

The Upper Mottled Limestone is a mottled light grey limestone, the mottling being of a blue or buff colored character. Lithologically this rock differs from the Lower Mottled rock in the presence of chalky nodules which can be picked out with the fingers from the lighter colored parts of the rock. Seventy-five fossil species have been identified from this formation.

The Stony Mountain formation consists of shales and limestones containing numerous fossils, sixty-one species having been identified.

The *Virgiana decussata* zone is composed of a harsh dolomite, buff to grey in color, and pitted from the dissolving of fossils. At Stonewall, Manitoba, a cross-bedded sandstone succeeded by a red clay is found at the base of the formation.

The position of the Gypsum beds as given in the stratigraphical table is doubtful being based on limited evidence.

The *Leperditia hisingeri* zone consists of a fine grained dolomite, greyish in color, and almost lithographic fineness. The top beds are red argillaceous dolomites on which the basal beds of the Devonian rest. Fossil material is not plentiful but in certain beds the ostrocod, *Leperditia hisingeri*, occurs in great abundance.

The Elm Point Limestone is typically a non-magnesian limestone, with argillaceous and arenaceous phases in its upper beds. The color is light grey to dark brown and shows in the Steep Rock quarry and elsewhere a mottled effect due to the presence of dark brown spots. Stylolytic structures are common. The formation is fossiliferous.

The Winnipegosan dolomite is a harsh porous dolomite of light grey or cream color and full of fossils. At its base is a red shale, and the transition to the Manitoba limestone is represented by a red argillaceous dolomite or shale.

The Manitoba limestone is lithologically similar to the Elm Point limestone. The color is greyish brown and the rock is very friable. No mottling has been noticed but stylolytic markings are common.

A discussion of the above formations has been made by Wallace[5], who gives a list of their fossil content.

The Winnipeg Sandstone, Gypsum beds, and Manitoba Limestone, will not be considered in this paper since dolomitization processes has played no part in their formation.

Discussion of the Formations Studied.

Upper Mottled Limestone.

The limestone of this formation is light grey in color and contains irregular dark brown or blue colored patches which gives to the rock its mottled appearance. These dark colored patches appear to be more strongly developed along the bedding planes than in other sections. A stronger development of them along jointing has nowhere been observed. Figure 1 is a photograph of a slab of the rock cut parallel to the bedding

[5] Wallace, R.C., Bull. Ntl. His. Soc. Man., 1925.

and shows the development of the structures in this plane. Figure 2 is a block of the limestone drawn to actual scale which shows more clearly the character of the mottling.

Wallace[6] has shown from a microscopic and chemical examination that the material composing the dark areas is dolomite.

Chemical Investigation: The light and dark areas were separated as completely as possible and subjected to chemical analysis to ascertain their difference chemically. The results obtained are given below with those obtained by Wallace[7] placed in the second column in each case.

Light areas.

SiO_2	1.02 per cent.	1.56 per cent.
Al_2O_3	0.25	0.06
Fe_2O_3	0.03	0.16
FeO	0.00	0.12
$CaCO_3$	94.41	94.02
$MgCO_3$	4.33	4.33

Dark areas

SiO_2	1.85 per cent.	1.56 per cent.
Al_2O_3	4.15	2.27
Fe_2O_3	0.63	1.94
FeO	0.43	0.45
$CaCO_3$	69.81	71.03
$MgCO_3$	23.31	23.35

The results, in both cases, are representative of a number

---

[6] Wallace, R.C., Jl. Geol., Vol. 21, 1913.

[7] Loc. Cit. p. 411.

made. Although there appears to be some disagreement in the individual percentages the general results are similar. The disagreement in the individual percentages is possibly explained by a more complete separation of the two materials having been obtained in one case.

The results of the analyses indicate that practically all of the iron and alumina have been introduced with the magnesian solutions, and the invariable presence of ferrous iron accompanying the magnesia suggests a reducing environment. They also substantiate the opinion previously referred to, that the dark colored areas are more dolomitic than the lighter parts of the rock.

The color difference between the blue and buff colored areas was shown by chemical analysis to be due to the percentage of ferrous iron present. The blue colored areas were found to contain almost double the quantity of ferrous iron present in the buff.

<u>Microscopic Investigation:</u> A striking difference in structure is noticed between the light and dark material under the microscope. The dark colored patches are composed of well formed crystals which give dolomitic reaction with Lemberg solution (see figure 3). The dolomite crystals are set close together and any hematite or limonite present is found separate from the dolomite and at the edges of the dolomite crystals. The hematite and limonite accounts for the color of the dolomitized areas and occurs in the light areas only where local dolomitization has taken place. The dolomitic areas show no trace of fossils. The lighter colored parts of the rock show numerous fragments

of brachiopods and sections of polyzoa and corals which are set in a fine grained calcareous matrix. Figure 4 is a microphotograph of the undolomitized portion of the rock.

The invariable association of the iron with the dolomite indicates that it was formed by the same agent that caused the dolomitization and probably contemporaneously.

Figure 5 is a microphotograph of the contact of the limestone with the dolomite.

Type of Dolomitization: Applying Dixon's[8] tests Wallace[9] concluded that the dolomitization in the area under discussion was of a contemporaneous nature. The dolomitization having taken place in a clear rather shallow sea with recurrent periods of slight mechanical sedimentation. The specific evidence in favor of contemporaneous dolomitization being that sections did not show any secondary calcification, borders of coral shells had not been attacked in preference to the matrix, and hematite was not included in the dolomite crystals.

Field evidence also points to contemporaneous dolomitization. The dolomitization has occurred throughout a depth of 97 feet without any stronger development being observed along the jointing planes than in any other vertical section. A gradation from a pure limestone through the mottled rock to a fully dolomitized stone has nowhere been observed. The Upper and Lower Mottled formations are overlain by the Stony Mountain and Cat Head beds respectively, which are more fully dolomitized. No shrinkage or slumping effects are present in the formation,

---

[8] Dixon, E.E.L., Quart. Jl. Geol. Soc., Vol. XVII, 1911, p. 447.

[9] Loc. Cit., p. 407.

effects which commonly would be expected in formations subsequently dolomitized. The contact between some fossils and the dolomite is an extremely sharp one indicating that no volume change had occurred during the change to dolomite. In this connection any volume change that had occurred when the unconsolidated ooze was dolomitized would be lost.

Structural Features of the Markings: A knowledge of the structural form of the dendritic areas is nescessary before any explanation of their origin can be attempted. This is especially the case as the proposal has been made to refer them to fucoidal structures. Consequently a detailed study of them has been made.

The dolomitic markings are connected horizontally and vertically forming an irregular but continuous connected pattern throughout the rock. It will be noticed that the vertical continuity is directly at variance with the conclusion of Wallace,[10] who states that, " the affected areas," are "unconnected vertically." The establishment of this fact was a matter of considerable difficulty, several methods being employed. Parallel sections of the rock were obtained at intervals of one-twentieth of an inch, by a process of abrasion. From tracings and photographs made of these surfaces, reconstruction of the three dimensional form of the mottlings was attempted. For various reasons this method proved unsatisfactory.

Ultimately advantage was taken of the difference in solubility between calcite and dolomite in dilute hydrochloric

10. Wallace, R.C., Loc. Cit., p. 412.

and acetic acids. Out of this a process was evolved which gave highly satisfactory results. Experiment showed that the best results could be obtained by using a five percent solution of both acids. The rock was first put into the hydrochloric acid solution and allowed to remain for two hours. It was then taken out, washed, and again submerged, this time in the acetic acid solution, for a period of time varying from ten to twenty hours, when the dolomitic material was left in suitable relief. Figures 6 and 7 are photographs of a block of the limestone (actual size) after treatment with the acids, and indicates clearly the vertical and horizontal connection of the patches. Figure 8 is a drawing, to actual scale, of a block of the limestone in which a piece has been cut out. This figure also indicates the three dimensional character of the darkareas.

A feature which may be of considerable significance is the fact that each patch or ramification contains at least one small vacant or calcite filled cavity (see figure 9) elongated in form, and dipping at a slight angle to the bedding plane. This feature is doubtless the "darker core" refered to by Wallace (see page 12). The cavities are confined entirely to the dark patches most of them tending to lie towards the centre of the undolomitic area. The continuous length of these tubes is unknown but the portions of them visible on any plane surface average in length between ¼ and ½ of an inch. The greatest length observed approximates 2 inches. The average diameter is between 1/8 and 1/16 of an inch. Their size or number does not appear to be proportional to the size of the patch they are confined to. Although these tubes are more or less straight it has been noticed that when they lie within the shell of a gastropod they tend to follow the curvature of the shell (see page 13 also figs. 10 and 14). Microscopic study shows a marked concentration of dolomite in the immediate vicinity of each tube which is also indicated by a darker color as seen macroscopically.

Relationship of the Dolomite to Fossils: Except in the vicinity of fossils the dolomitic material show diffuse or indefinite boundaries, grading almost imperceptibly into the limestone matrix. The relationship of the dolomitic patches to fossils on the other hand, is always a definite one. Where fossils are involved hard contacts or definite boundaries are always observed. Certain types of fossils are entirely unaffected in contact with the dolomite while others are partially or completely altered to that material.

The structure of corals, stromatoporoids, bryozoans, and brachiopods, never shows this alteration although these fossils are frequently almost or completely surrounded by mottling (see figures 10 and 11). The mottlings, however, often penetrate the interspaces within the structures of the fossils as for instance within the calyx and interseptal spaces of the large cup coral Streptelasma (see figure 10) or again, the rock matrix between the chains of corallites of Halysites. Spaces between the layers of stromatoporoids also are liable to be similarly affected (see figures 11 and 12).

The case of gastropods and cephalopods is entirely different. These fossils commonly show within their structures the very strongest concentration of the dolomitic material (see figure 10). A mottled ramification whenever it meets one of these fossils immediately loses its indefinite outline and becomes confined within the definite boundaries of the shell structure (see figures 10, 13, and 14). This point is particularly well illustrated in figure 13 where a large patch merges with the apex of a tall spired gastropod. In this particular instance it will be noticed that in addition to the shell wall the rock matrix within the apical whorls is also dolomite.

Dolomitization of the outer shell walls of the cephalopods, which are so abundant in the limestone, is practically universal, while the septa are to a greater or less extent affected (see figures 15, 16, and 17). Mottling is frequently observed within the chambers of the shells where the septa commonly define the boundaries of such mottling. For example in figure 15 there are several points shown within the large straight shell where one or several chambers in succession are occupied by the dark rock, followed by others which are composed of the normal grey limestone. In these cases the relationship of septa to the boundaries of the mottlings will be clearly seen.

These observations can be readily verified by reference to the surfaces of the cut stone in buildings which are made of this Upper Mottled limestone. In these will be found abundant illustrations of the points noted here.

<u>The Fucoidal Theory:</u> The fucoidal theory of origin for the dendritic markings has been suggested by Wallace[10] who states, "Only from such organisms and allied types could the percentage of Mg salts be increased locally to any appreciable extent. There are certain structural features of the markings that lend some support to this view of the origin of the dolomit-

[10] Loc. Cit., p. 416.

-ization. They are horizontally placed, are markedly dendritic, and the sections often show a darker core which might represent the actual position of the plant; while the magnesian waters, extending outward from this central nucleus, have affected the surrounding stone."

Mr. Setchell of the University of California was kind enough to examine sections of the dolomitic material referred to him by the writer. As a result of his investigation he reported no organic structure to be recognizable. In this connection it must be remembered however, that the absence of recognizable organic structure does not nescessarily preclude fucoidal origin, since chemical alteration (such as would be invâlved in a process of dolomitization) would obliterate such structure.

Wallace[11] has already pointed out the absence of a rocky bottom as a difficulty in the acceptance of extensive growth of brown algae. His statement of the essentially horizontal position of the dendritic markings has been met by the demonstration of their extension in the vertical plane (see page 9). If on the other hand these be regarded as representing calcareous algae it might be argued that such plants, possessing a certain degree of rigidity, might remain in their position of growth during a fairly rapid accumulation of calcareous ooze around them. But the nature of the "fronds" themselves, which are often of great length, show branching of entirely irregular character and frequently rejoin, seems to militate against any theory of algal origin. Certainly in no way are these structures similar to the undoubted algal remains first

[11] Loc. Cit., p.417.

described by Whiteaves[12] from the Cat Head and Stony Mountain formations. This will readily be seen by a comparison of figure 1 with figure 18 or 19.

It should also be pointed out that the dendritic markings are remarkably uniform for a depth of 97 feet, and also, so far as observation goes, over a very wide lateral area. Such extensive growth of a single plant type, without any physical break, seems highly improbable.

It is, however, principally on the basis of the evidence already given in the section dealing with the relationship of the dolomite to fossils that the fucoidal theory must, in the opinion of the writer, be abandoned.

It has been shown for instance that some of the fossils, such as corals, are completely surrounded by the markings even to the degree of penetration of their caliclular and interseptal spaces. The fossils themselves in such cases being apparently unaltered in composition; while, on the other hand, cephalopod and gastropod shells are actually penetrated and their walls and septa completely transformed to dolomite. As already shown, cases of dolomite points passing into and becoming localized within such shell walls are frequent. In fact this seems to be the universal relationship. Most significant of all is the fact that the tubular cavities or dark core (which Wallace thought might represent the actual position of the plant) of the dolomite areas have actually been seen <u>within</u> the walls of gastropod shells; not penetrating them transversely, but following their outlines. Such a relationship of algal plants to hard calcareous shells is impossible.

[12] Whiteaves, J.F.G., G.S.C., Vol. III, pt. III, 1897.

It appears therefore that the fucoidal theory cannot be made to meet the facts and hence one is forced to look elsewhere for a solution of the problem. Hawley[13] has shown that such structures are possible by purely inorganic agencies.

Origin of the Mottling: The evidence at hand points to the action of diffusing solutions as having been an important factor in the formation of the dendritic markings. The tubular cavities with a concentration of dolomite about them have apparently acted as centres from which the dolomitization started. In the section discussing the relationship of the dolomitic markings to fossils it was pointed out that corals, brachiopods, bryozoans, and stromatoporoids are unaltered, while gastropods and cephalopods are almost or completely dolomitized. It appears therefore, that the dolomitization has, in the case of the fossils in the first named group, met with definite opposition; while those named in the second group, in whose composition aragonite in all probability played an important part, have been partial to dolomitization. Since the fossils of both groups were essentially composed of calcium carbonate it could not have been the chemical composition of the shells which was the determining factor. It is well known that calcium carbonate in the form of the mineral aragonite is much more susceptible to chemical reaction, and consequently to dolomitization, than is calcium carbonate in the form of the mineral calcite. Skeats[14] in his study of dolomitized coral reefs found that the

13. Hawley, J.E., Jl. Geol., Vol. 34, 1926, p. 441.

14. Skeats, E.W., Am. Jl. Sc., Series 4, Vol. 45, 1918, p. 192.

formation of dolomite crystals proceeded along definite lines, aragonitic organisms being dolomitized before those of calcite and the structureless matrix first of all. If then the fossils which have been dolomitized, in the area under discussion, were originally composed of aragonite, while those that have remained unchanged, were originally composed of calcite, we have a ready explanation of the selective dolomitization in the case of the fossils. Following this idea farther, it may have been that small fragments of aragonitic shells acted as the centres from which the dolomitization started in the calcareous ooze the solutions altering all the material that was not composed of calcite and producing a mottled rock.

Source of the Magnesium: Experimental evidence shows that high concentrations of magnesium sulphate and magnesium chloride favor the change from calcite to dolomite. There is no evidence that the sea of Upper Mottled times was a landlocked one as the reaction products, gypsum and salt deposits, usually present where dolomite has formed under concentrated conditions are absent. The sea may have possessed a salinity higher than oceanic waters of the present day, but as corals were present which were very delicately adapted to their environment, high concentrated conditions would have doubtfully obtained.

Ordinary concentrations of sea water are adequate to cause dolomitization and many examples have been cited[15]. Weller[16] from a faunal comparison of two contemporaneous formations, one limestone and the other dolomite, concluded that the waters of the dolomitic formation had not been more saline, warmer, or shallower than the sea in which the limestone had been laid down.

It would appear that relatively minor changes in either the physical or chemical condition of the sea, or both, must have been sufficient to cause the formation of dolomite. It is known that at atmospheric pressure magnesium carbonate is more soluble than calcium carbonate and that at 4 atmospheres of CO_2 the reverse is true. Skeats[17] concludes from these facts that the most favorable conditions for the formation of dolomite obtain (under suitable conditions of saturation) at some point between 1 and 4 atmospheres of pressure, that is under relatively shallow water conditions. At that point the two carbonates would be expected to precipitate in molecular proportions readily available for the change to dolomite. Thus it may have been that in the formations studied by Weller the dolomitic facies represent a slight shallowing of the sea, the physical change not being sufficiently great to acuse a change in the fauna present.

The Upper Mottled limestone was laid down in a relatively shallow sea under reducing conditions, as indicated by the invariable presence of ferrous iron with the dolomite. It therefore must have been the lower strata of sea water that constituted the important dolomitizing agent, since ferrous iron in aqueous solution is veryeasily oxidized. Wave

---

15. Clarke, F.W., U.S.G.S., Bull. 770, 1924, p. 575.
16. Weller, S., Bull. G.S.A., Vol.22, 1911, pp. 227-231.
17. Loc. Cit., p.199.

action may have areated the water but the gases of decay may habe excluded it from the lower strata of water. It is possible that at this point the magnesium percentage of the water may have been increased by the extraction of calcium salts by calcium secreting animals. Various analyses of oceanic waters of to-day indicate the percentage of magnesium salts to be four times that of calcium. Thus if the magnesium percentage be increased in some manner, such as suggested above, dolomitizatin might take place, if suitable conditions of temperature and pressure obtained. Under such conditions the change to dolomite would be expected to require a long time under stable conditions. Relatively minor changes in the conditions of deposition causing limestone or dolomite to form depending upon the direction in which the equilibrium of the sea was shifted. In this connection it is interesting to note that the Upper Mottled limestone is underlain and overlain by more fully dolomitized horizons.

<u>Summary and Conclusion</u>: The results of this investigation supports the views of Wallace that the dendritic markings are due to partial contemporaneous dolomitization that has taken place in a reducing environment; but finds that the fucoidal theory of origin cannot be made to fit the facts. It is, in the opinion of the writer, principally on the basis of the relationship of the dolomitic patches to fossils, that the fucoidal theory of origin must be abandoned. It is suggested that the dolomitization is due to diffusing solutions. The selective dolomitization of fossils has been explained on the assumption that the aragonitic ones have been altered. The lower

strata of sea water are considered to have been the impprtant dolomitizing agent, which has had its magnesian content increased to such an extent that, under suitable conditions of temperature and pressure, dolomitization could take place.

Lower Mottled Limestone.

The limestone of this formation is characteristically mottled, the mottling being similar to that present in the Upper Mottled rock. The mottling of the Lower Mottled formation was not investigated as exposures of the rock are remote and samples difficult to obtain. Since the markings present in the two formations possess similar characteristics it is probable that any explanation of the dendritic markings in the Upper Mottled limestone will apply to these of the Lower Mottled limestone as well.

An analysis of the Lower Mottled rock, in which the light and dark areas had not been separated, is given below.

SiO_2 .... 6.21 per cent.
Fe_2O_3 & Al_2O_3 ... 1.33
$CaCO_3$ 76.21
$MgCO_3$ 16.10

Cat Head Limestone.

The Cat Head formation consists of a fine grained fully dolomitized limestone with an even yellow color and nowhere exhibiting a mottled affect characteristic of the limestones which lie above and below it. The formation is recognized by the presence of chert nodules which are found throughout the beds but more particularly at the base of the formation. The large cephalopods of the Lower Mottled limestone are wanting, but the formation is unusually rich in fucoidal remains, several species having been identified(see figs. 18 and 19).

Chemical Investigation: Samples of the rock were subjected to chemical analysis, the results given below being representative of a number made.

SiO_2	1.02 per cent.
Al_2O_3	0.75
Fe_2O_3	0.17
FeO	0.01
$CaCO_3$	75.51
$MgCO_3$	22.42

Microscopic Investigation: Under the microscope the rock is seen to be composed of well crystallized rhombohedrons of dolomite containing many dusty inclusions(see fig. 20). Iron is present as interstitial hematite which in no case was observed to be zonal. No fossil materialwas present in the sections studied.

Conclusions: The results of the chemical and microscopical investigation show the rock to be a dolomite. The color of the dolomite is due to the presence of interstitial hematite.

Stony Mountain Formation:

The Stony Mountain formation as described by Dowling[18] consists of limestones and shales. The series is well exposed in the quarries at Stony Mountain, Manitoba. The limestone is porous, yellow in color, and in places exhibits a mottled

---

[18] Dowling, D.B., G.S.C. Bull. 704, 1900, p. 46 F.

effect due to the presence of brown patches in the yellow groundmass. Most of the fossil material from this formation has been found in the shales at the base.

<u>Chemical Investigation</u>: Samples of the mottled rock were obtained from the "Upper" and "Lower" beds, and subjected to chemical analysis. The material causing the mottling and the groundmass were separated as completely as possible and and analyzed separately in both cases. The results obtained are given below.

Upper Beds.

	Light	Dark.
SiO_2;......	2.50 per cent.	1.65 per cent.
Al_2O_3......	7.33	7.04
Fe_2O_3......	0.17	1.20
FeO	0.00	0.26
$CaCO_3$......	59.56	53.04
$MgCO_3$......	30.04	36.58

Lower Beds.

	Light.	Dark.
SiO_2.......	1.73 per cent.	0.98 per cent.
Al_2O_3......	3.05	3.31
Fe_2O_3......	0.19	1.21
FeO........	0.00	0.10
$CaCO_3$......	54.78	51.09
$MgCO_3$......	40.06	43.06

The analyses indicate that as a whole the upper beds are more argillaceous than the lower, containing a higher percentage of silica and alumina. Both beds contain a high percentage of magnesium carbonate, while the dark areas in each case possess a greater concentration of magnesium, ferric and ferrous iron, than does the light. In the case of the lower beds the dark areas also show an increase in alumina, the upper beds on the other hand show a decrease.

<u>Microscopic Investigation</u>: Under the microscope sections from the upper beds show well defined rhombohedra of dolomite, although many crystals do not exhibit their characteristic shape due to mutual interference during growth. All of the crystals contain many dusty inclusions. Iron is present as interstitial limonite and hematite which accounts for the color of the rock. There is no well defined boundary between the light and dark areas, but the dark areas contain a greater concentration of iron.

The above information also applies to the lower beds which are slightly finer grained. Figures 21, 22, 23, and 24 are microphotographs from the upper and lower beds. In these will be seen the points noted here.

No fossil material was present(recognizable as such) in any of the sections studied.

<u>Conclusions</u>: The microscopic and chemical examination show the rock to be an argillaceous dolomite in both cases. The mottled areas are more fully dolomitized than the lighter ones and owe their color to the concentration of iron which has occurred within them. It would appear that the magnesian solutions had carried iron and in the case of the lower beds alumina also.

Virgiana decussata Zone.

The Virgiana decussata zone consists of very compact, fine grained dolomites, buff and grey in color. They are not rich in fossil material but the rock is often pitted due to the dissolving of fossils.

Chemical Investigation: Chemical analysis indicated the rock to approach closely the composition of normal dolomite. A representative result is given below.

SiO_2	0.58 per cent.
Al_2O_3	0.41
Fe_2O_3	0.20
FeO	0.04
$CaCO_3$	55.00
$MgCO_3$	43.67

Microscopic Investigation: Under the microscope the rock is seen to be very fine grained showing a granular mosaic structure composed of small crystals of dolomite and devoid of recognizable fossible material(see figure 25). Iron is present as interstitial matter which was nowhere observed to be included centrall or zonally in the dolomite rhombohedrons. The dolomite crystals are colorless containing many dusty inclusions.

Conclusion: The chemical and microscopical examination show the rock to be practically a pure dolomite, apparently devoid of fossil material, and owing its color to interstitial hematite.

Leperditia hisingeri Zone.

The *Leperditia hisingeri* zone consists of very fine grained greyish colored dolomites containing little fossil material.

Chemical Investigation: Samples of the rock were subjected to chemical analysis the result given below being representative of a number made.

SiO_2	1.27 per cent.
Al_2O_3	0.41
Fe_2O_3	0.08
FeO	0.05
$CaCO_3$	54.12
$MgCO_3$	43.50

Microscopic Investigation: Under the microscope the rock is seen to be very fine grained composed of small cloudy crystals of dolomite which are evenly crystallized(see fig. 26). Iron occurs principally as interstitial hematite, but some limonite is present coating some of the dolomite crystals. No fossil material was fecognized in any of the sections studied.

Elm Point Limestone.

The rocks of this formation are characteristically mottled due to the presence of dark brown spots in the light grey limestone(see figure 27). The dark patches are rounded and, so far as known, are not more strongly marked along the bedding planes than in other sections. Many of the spots are connected horizontally and vertically but they do not form a continued connected pattern throughout the rock. Fossil material is not confined to any one area but occurs in both the light grey limestone and dark patches. The character of this mottling is quite different from that of the Lower and Upper Mottled formations as can readily be seen by comparing figure 27 with figure 1. The block of limestone in figure 27 was treated with hydrochloric acid to bring out the spots more clearly for photographic purposes. During the process of acid treatment air was bubbled through the solution which caused the formation of the corrugated structure as seen in the figure. Figure 28 is a drawing to actual scale of a block of the limestone showing more clearly the type of mottling in this limestone.

Chemical Investigation: In order to ascertain the chemical difference between the light and dark area they were separated and separately analyzed. The results obtained are given below.

	Light.	Dark
SiO_2............	0.85 per cent.	0.31 per cent.
Al_2O_3..........	0.52	0.52
Fe_2O_3..........	0.13	1.41
FeO............	0.13	0.03
$CaCO_3$..........	95.88	95.80
$MgCO_3$..........	2.77	1.89

The chemical analyses indicate a low percentage of magnesium carbonate in both areas with a slightly higher concentration is noted in the lighter parts of the rock. A definite increase in the iron percentage is noted in the darker areas but most of the ferrous iron is present in the light areas where the concentration of magnesium carbonate occurs. The higher percentage of silica in the lighter areas may be due to the presence of siliceous shells.

<u>Microscopic Investigation:</u> Under the microscope both areas were found to be composed of a fine grained calcareous matrix containing numerous sections of crinoids, polyzoa, brachiopods and corals(see figures 29 and 30). Iron in the form of hematite was confined mainly to the dark areas which possessed a gradational contact with the calcareous matrix(see figure 31).

<u>Conclusions:</u> The microscopic and chemical examination indicates the rock to be a magnesian limestone. The mottled character is due to the presence of iron which has become ~~localized~~ concentrated in localized areas. Dolomitization has apparently played no part in the formation of the darker areas, the solutions carrying the iron having carried no magnesium. The iron was probably carried in the form of ferrous carbonate which replaced the limestone and has later been oxidized to limonite.

<u>Winnipegosan Dolomite</u>.

Samples of the grey and cream colored dolomite which occurs in this formation were subjected to chemical analysis, the results given below being representative of a number made.

SiO_2...........	1.65 per cent.
Al_2O_3..........	0.26
Fe_2O_3..........	0.02
FeO............	0.08
$CaCO_3$..........	56.01
$MgCO_3$..........	41.85

Under the microscope sections of the rock are evenly crystallized, showing idiomorphic colorless rhombohedra with many dusty inclusions (see figure 32). The crystals of dolomite are set close together and the rock appears to be devoid of microscopic fossil material. All iron that occurs does so as interstitial hematite, none being present as zonal or central inclusions in the dolomite crystals.

The chemical and microscopic investigation show the rock to approach the true composition of dolomite.

Mottled Limestone Boulder from Gimili Manitoba.

A limestone boulder picked up on the beach at Gimili Manitoba possessed a mottled appearance unlike any noticed in the palaeozoic rocks of Manitoba.

The mottled effect is due to the presence of blue colored areas in the light grey limestone. The blue patches are irregularly shaped and appear to have an outer and inner wall whcih are separated by the normal light grey limestone. The space surrounded by the inner wall is almost or entirely of the blue material. Figure 33 is a photograph of the boulder and shows the mottling referred to.

Chemical Investigation: Analyses of the dark and light portions of the stone gave the results listed below.

	Light.	Dark.
SiO_2..............	1.02 per cent.	1.21 per cent.
Al_2O_3.............	7.67	8.09
Fe_2O_3.............	0.85	2.10
FeO...............	0.78	1.04
$CaCO_3$.............	57.98	53.61
$MgCO_3$.............	31.43	33.53

The analyses indicate a greater concentration of iron (ferrous and ferric), magnesia, and alumina in the dark areas.

Microscopic Investigation: In thin section the light and dark areas are composed of rhombohedrons of dolomite, although many of the crystals do not show their characteristic shape due to the mutual interference during growth. Practically all of the iron occurs in the dark areas as interstitial hematite. The contact between the two areas is gradational and neither of them, in the sections studied, contained any fossil material or organic structure

Conclusion; The chemical and microscopic investigation shows the rock to be a dolomite, the darker areas possessing a higher percentage of iron, alumina, and magnesia.

Summary and Conclusions.

The investigation has been confined to those rocks which possess a mottled appearance or have suffered changes by dolomitization. A note has been added on a mottled drift boulder from Gimili Manitoba which possessed a peculiar mottled structure. The Upper Mottled limestone of the Ordivician has been dealt with in greatest detail as the rock is well exposed near Winnipeg where its characteristics in the field could be studied in conjunction with the laboratory work. Field information is lacking in the case of other formations making it impossible to reach any definite conclusions regarding the dolomitization at this time.

In the case of the Upper Mottled limestone the views of Wallace that the mottling is due to partial contemporaneous dolomitization are substantiated but disagrees with his suggestion of fucoidal origin. The relationship of the dendritic markings to fossils with other facts strongly opposes the possibility of fucoidal origin. The evidence at hand indicates that the dolomitization has been a diagenetic process taking place along definite lines, the structureless matrix and aragonitic shells having been altered. Fossil material composed of calcite has remained unchanged. The color of the patches is due to [illegible] interstitial limonite and hematite while in the blue colored patches the ferrous iron percentage has been a determining factor.

The mottling present in the Stony Mountain formation and the limestone drift boulder is shown to be due to dolomitization, the dolomitizing solutions having carried iron which has become concentrated in localized areas. In the case of the mottled Elm Point limestone it is shown that dolomitization has apparently played no part the darker areas carrying only a higher percentage of iron. It would thus appear that magnesium solutions always carry iron but that iron can be carried alone. The ferrous iron present does not appear to be proportional to the magnesium carbonate, but in the partially dolomitized rocks an increase is noticed in the dolomitic areas.

An interesting feature of the fully dolomitized rocks is that under the microscope they are composed entirely of dolomite crystals which contain many dark inclusions, and yet, while many of them contain in excess of forty percent magnesium carbonate, none have the composition of a true dolomite. Since all of them contain a surplus of calcium carbonate over that required in a true dolomite, it may be that the dusty inclusions in the dolomite crystals is calcite.

Neither the partially dolomitized or fully dolomitized rocks contain recognizable fossil material. The rocks were formed under marine conditions and it is certain that marine life was present. The conclusion is therefore reached that the process of dolomitization has obliterated the smaller fossils, the formations now containing only the larger and more robust types.

Bibliography of Dolomitization.

1. Blackwelder, E., Origin of the Bighorn Dolomites of Wyoming, Bull. G.S.A., Vol. 24, 1913, p. 607.

2. Clarke, F.W., U.S.G.S. Bull. 695, 1920, pp. 557-578.

3. " " " 770, 1924, pp. 565-580.

4. " & Wheeler, W.C., U.S.G.S. PP. 90D? 1914, p. 33 & 91.

5. " " The Inorganic Constituents of the Marine Invertebrates, U.S.G.S. PP. 124, 1922.

6. Daly, R.A., Metamorphism and its phases, Bull. G.S.A., Vol. 28, 1917, pp. 375-418.

7. Davis, N.P., The character and possible origin of the green dolomites of New Ontario, C.I.M. Jl., Vol. 14, 1912, pp. 678-689.

8. Dixon, E.L., The Geology of the South Wales Coal Fields, Mem. 247, Pt. 8, 1907, Geol. Sur. Eng. & Wales.

9

9. Grabau, A.W., Primciples of Stratigraphy, pp. 758-762.

10. Hall, C.W., & Sardeson, F.W., The Magnesian Series of the Northwestern States, Bull. G.S.A., Vol. 6, 1895.

11. Hewett, D.F., Dolomitization in Southern Nevada, G.S.A.Ab. 1923

12. Van Hise, Treatise on Metamorphism, U.S.G.S. Mon. 47. p.798.

13. Klement, R.C., Sur l'Origine de la Dolomie dans les Formations Sedimentaires. Bull. d.l. Soc. Belge d. Geol. Tome IX, 1895, pp. 3-23. Review In Geol. Mag. 1895.

14. Dale, T.N., The Lime Bwlt of Massachusetts and Part of Eastern New York and Western Connecticut, U.S.G.S.; Bull. 744, 1923.

15. " The Commercial Marbles of Vermont, U.S.G.S. Bull. 521, 1912.

16. Parsons, L.M., Dolomitization and the Leicestershire Dolomites, Geol. Mag., Vol. 5, 1918, pp. 246-258.

17. " Dolomitization in the Carboniferous Limestones of the Midlands, Geol. Mag.Vol. 59, 1922, p. 501.

18. Peach & Horne, The Geological Structure of the Northwest Highlands of Scotland, Geol. Sur. Gt. Br. Mem. 379,

19. Skeats, E.W.? The Formation of Dolomite and its Bearing on the Coral Reef Problem, Am. Jl. Sc. Vol. 45, 1918.

20. " On the Chemical and Mineralogical Evidence as to the Origin of the Dolomites of Southern Tyrol, Jl.Geol. Soc. Vol. 61, 1905, p.97.

21. Skeats, E.W., The Chemical Composition of Limestones from Upraised Coral Reefs with Notes on their Microscopical Structures., Bull. Mus. Comp. Zool. Harvard, Vol. 42, 1903, pp. 53-126.

22. Steidtman, E., The Evaluation of Limestone and Dolomite, Jl. Geol. Vol. 19, 1911, 323-345, & 392-428.

23. " Origin of Dolomite as disclosed by stains and other methods., Bull. G.S.A. Vol.28, 1917, p.431.

24. " Results of a study of Dolomitization., Sc. n.s. Vol. 44, 1916, pp. 56-57.

25. Tarr, W.A., Contribution to the Origin of Dolomite, Bull. G.S. A.(abs.), Vol. 30, 1919, p. 114.

26. Twenhofel, W.H., Treatise on Sedimentation., pp. 251-265.

27. Van Tuyl, F.M., The present Status of the Dolomite Problem., Col. School of Mines Mag. Vol. 7, # 11, p. 185, 1917.

28. " New Points on the Origin of Dolomites, Bull. G.S.A. Vol. 26, 1915, p. 62.

29. " Mottled Limestones and Their Bearing on the Origin of Dolomite., Sc. n.s., Vol. 43, 1916, 24.

30. " The Origin of Dolomite., Ia. Geol. Sur. Vol. 25, 1916, pp. 251-421.

31. " The Origin of Dolomites., N.Y.Acad. Sc. Annals, Vol. 24, 1915, p. 362-363.

32. " New Points on the Origin of Dolomite., Am. Jl. Sc. series 4, Vol. 42, 1916, pp. 249-260.

33. " The Present Status of the Dolomite Problem., Sc.n.s., Vol. 44, 1916, pp. 688-690.

34. " The Depth of Dolomitization., Sc. n.s., Vol. 48, 1918, pp. 350-352.

35. Wallace, R.C., A Contribution to the Study of Dolomitization., Proc. and Trans. Roy. Soc. Canada, 3rd. series, Vol. 7, Sect. 4, 1914, pp. 139-149.

36. " Pseudo-brecciation in Ordovician Limestones in Manitoba., Jl. Geol. Vol. 21, 1913, pp. 402-421.

37. " A Physico-chemical Contribution to the Study of Dolomitization., Intern. Geol. Cong. 1913, 875

38. Weller, S., Are the Fossils of the Dolomites Indicative of

Shallow, Highly Saline and Warm Water Seas? Bull. G.S.A. Vol. 22, 1911, pp. 227-231.

40. Wyckoff, R, & Merwin, H.G., The Crystal Structure of Dolomite., Am. Jl. Sc. 5, Vol. 8, 1924, p. 447.

Figure 1. Mottled Upper Mottled limestone parallel to bedding.

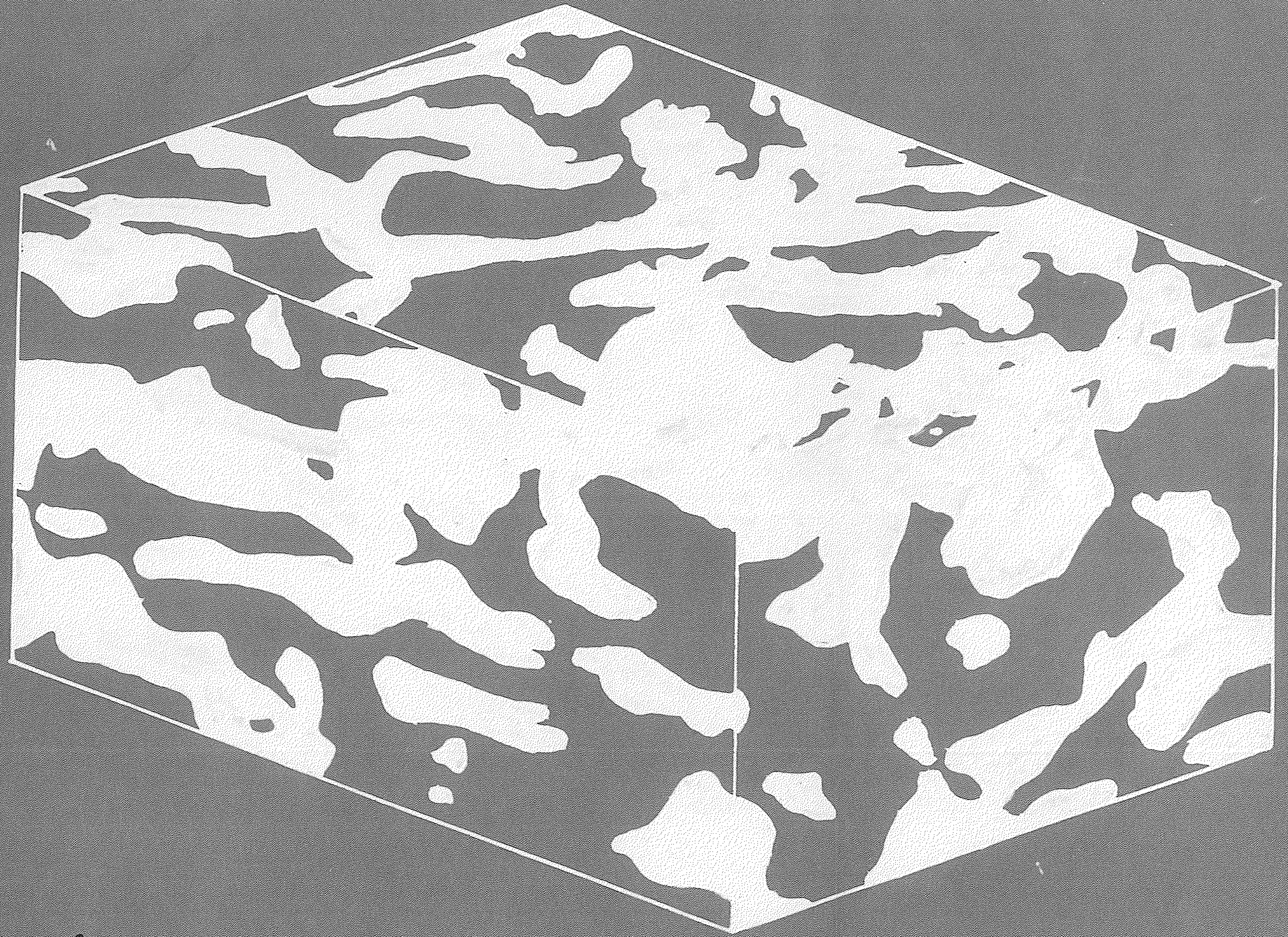

Figure 2.

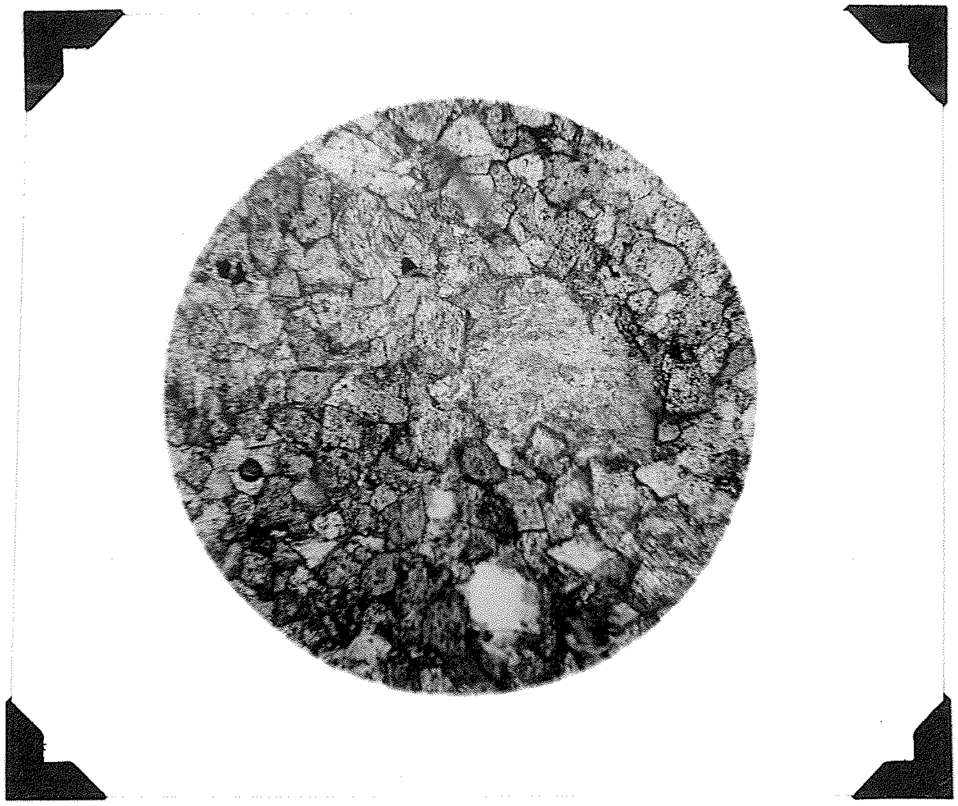

Figure 3. Dolomitized area of the Upper Mottled limestone.

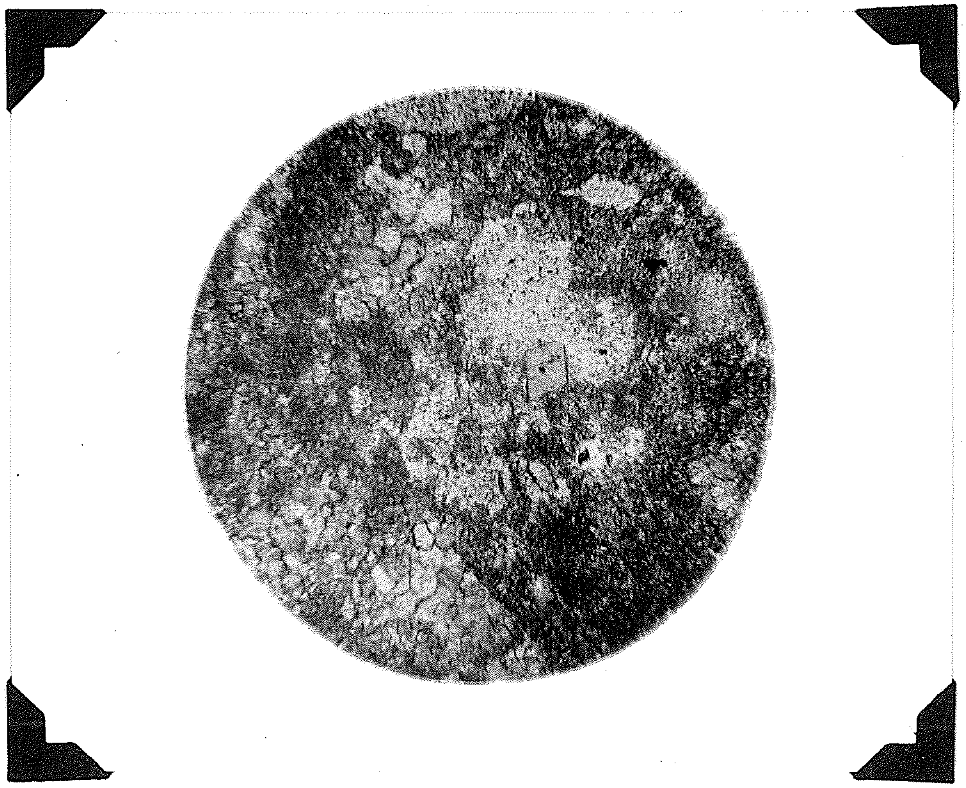

Figure 4. Undolomitized area of the Upper Mottled limestone.

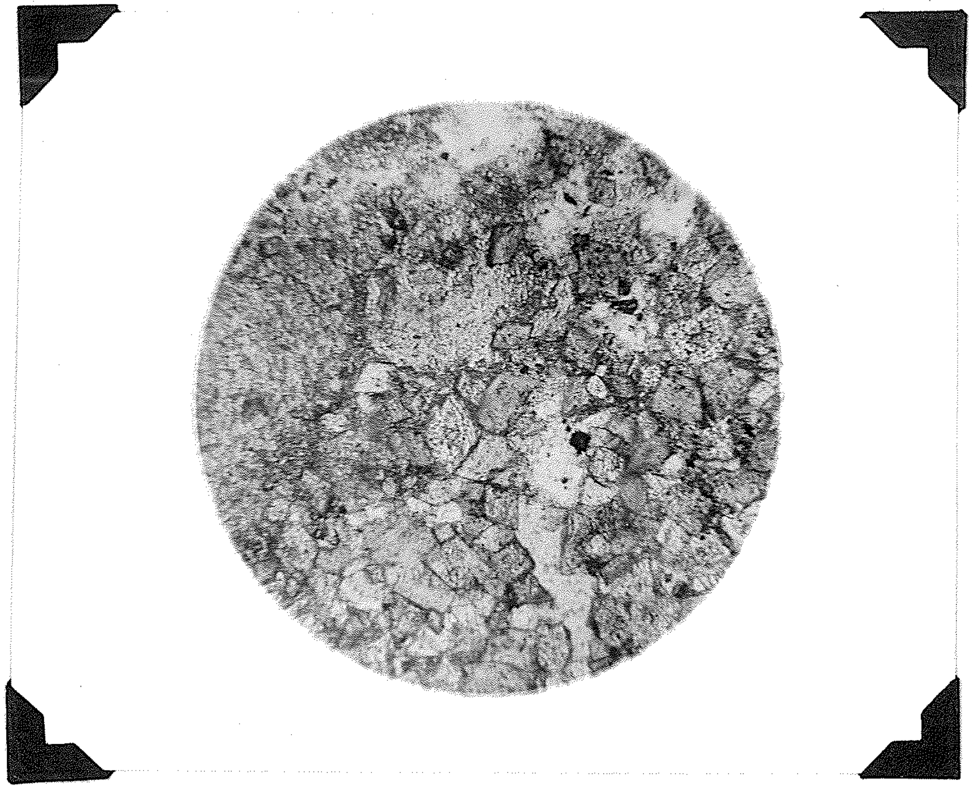

Figure 5. Contact of light and dark areas, Upper Mottled horizon.

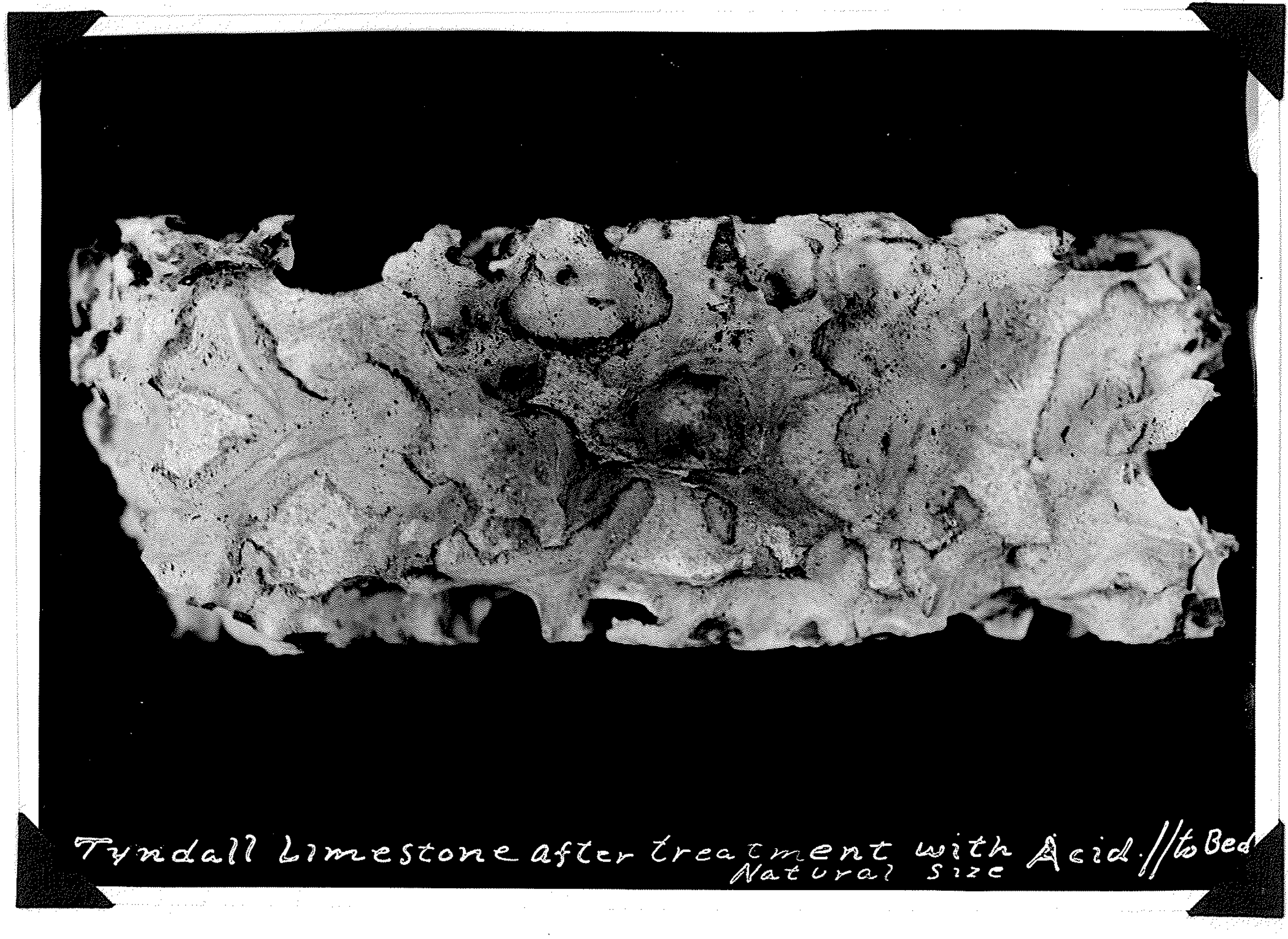

Figure 6. Upper Mottled limestone after acid treatment.

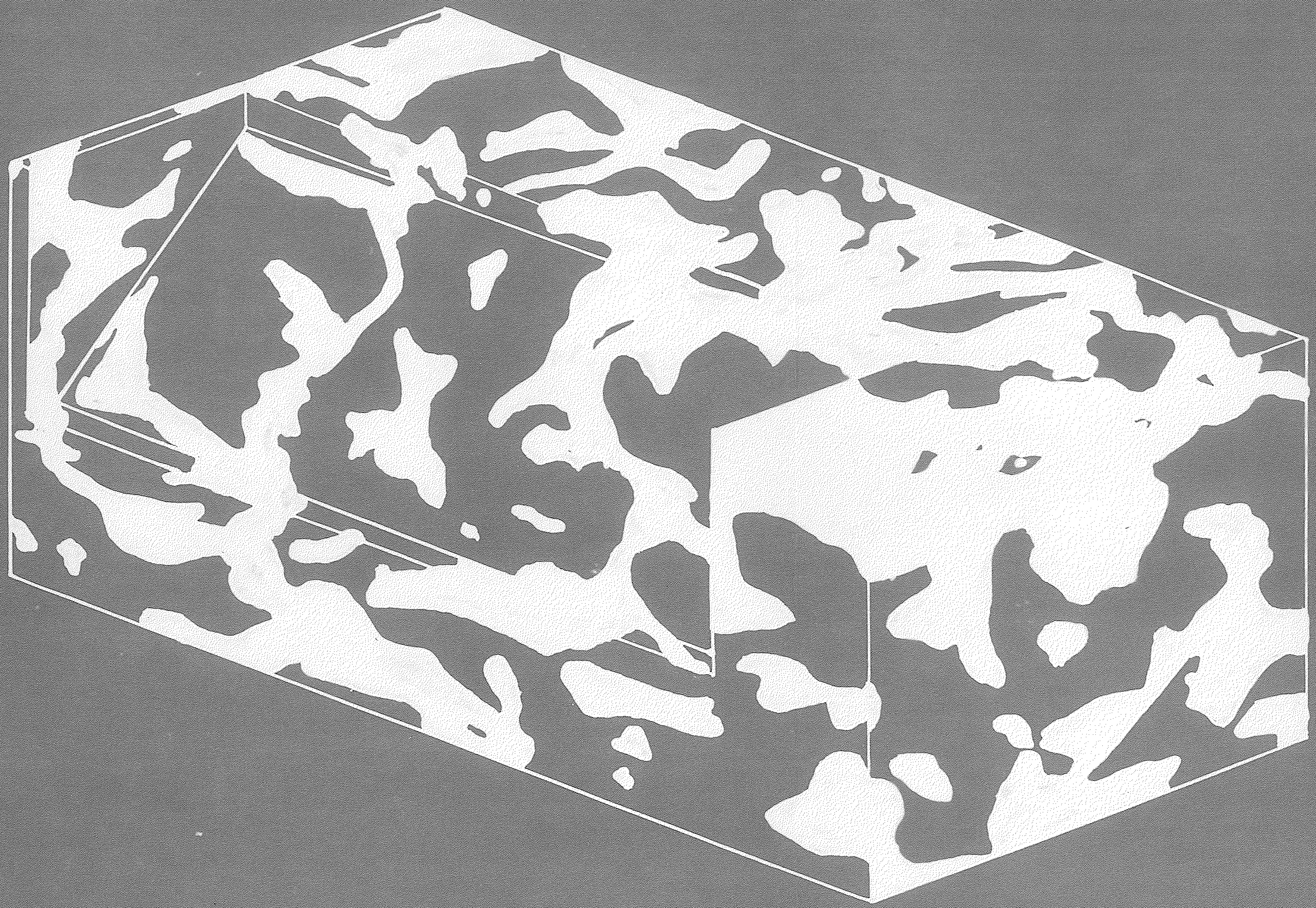

Figure 8.

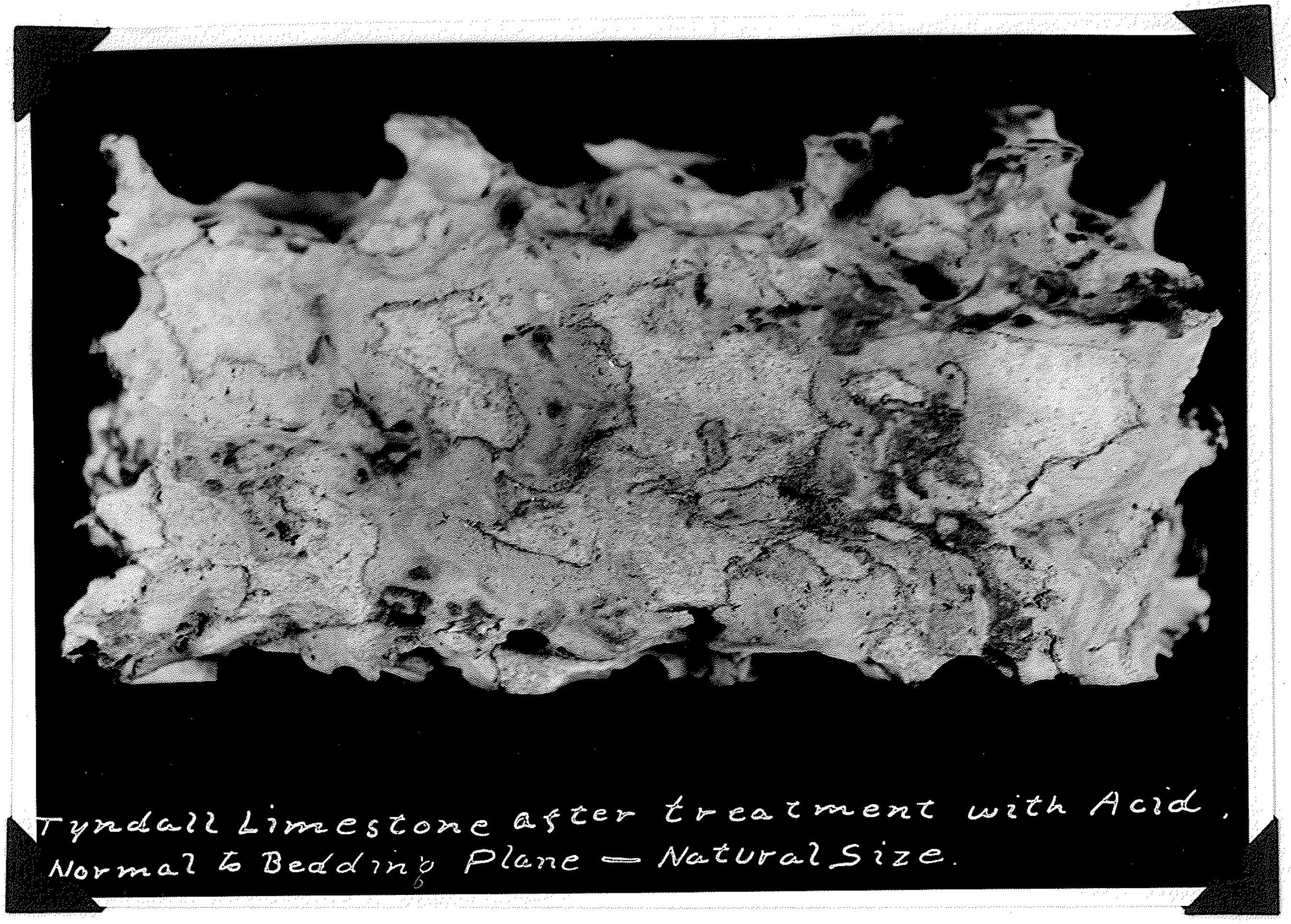

Figure 7. Upper Mottled limestone after acid treatment.

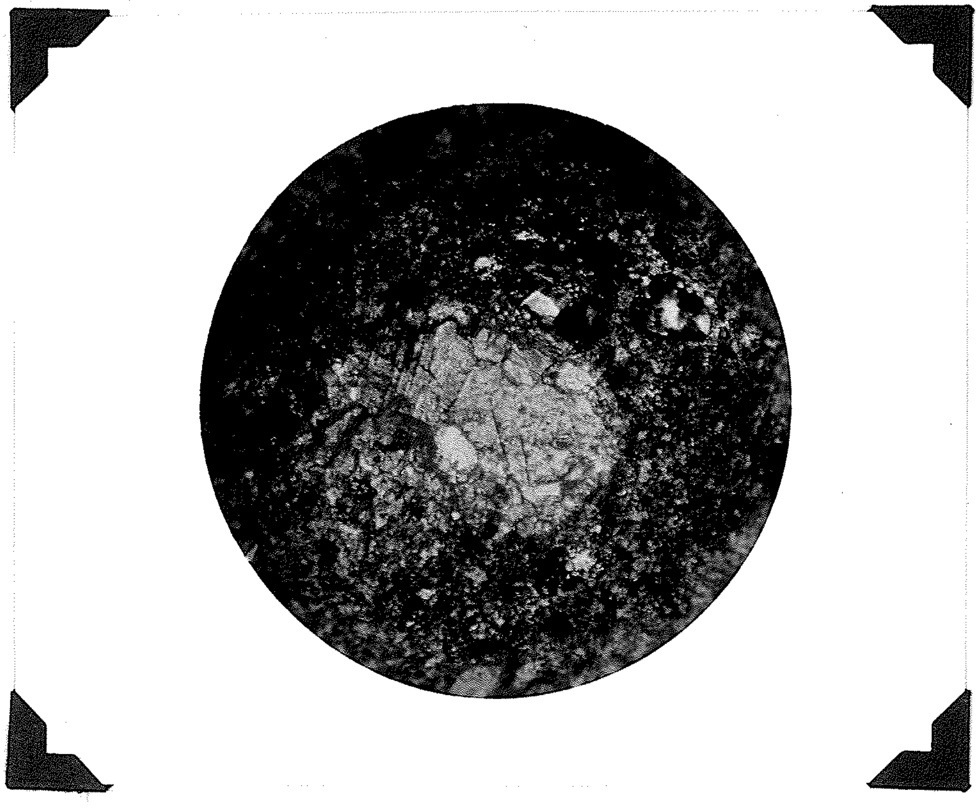

Figure 9. Section of "dark core" Upper Mottled limestone.

Figure 10. Upper Mottled limestone showing altered fossils.

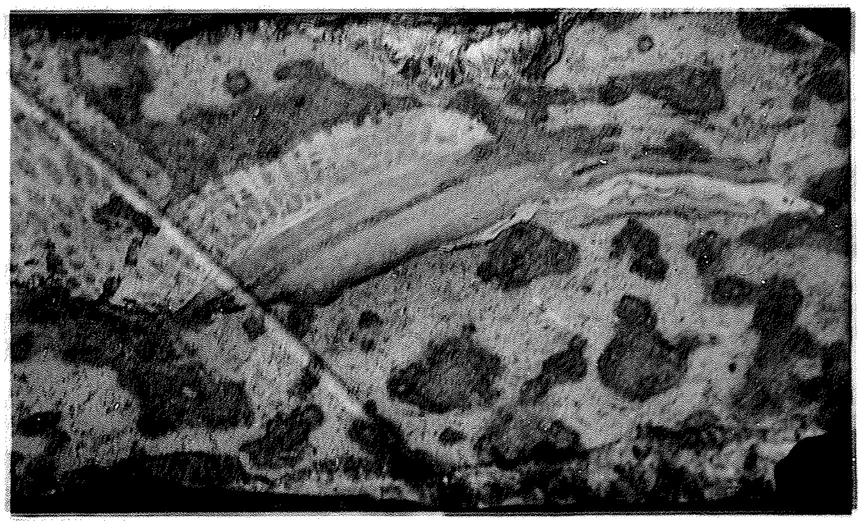

Figure 11. Showing relationship of dark areas to stromatoporoids.

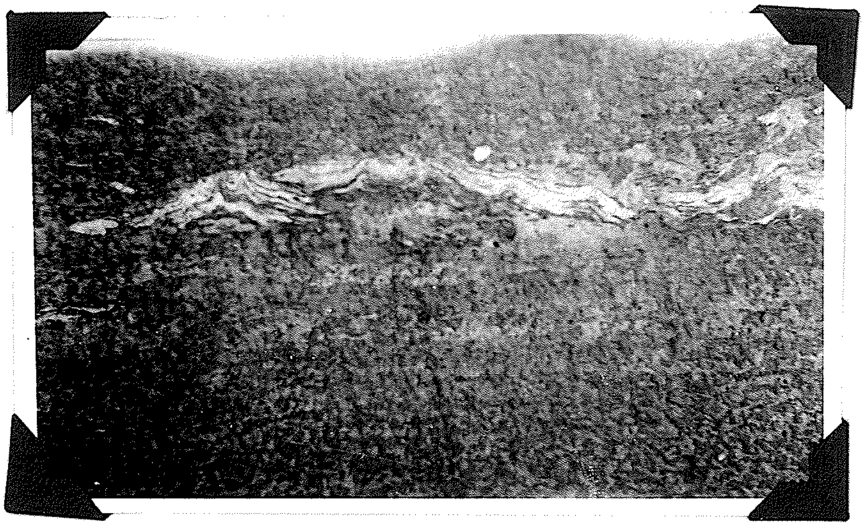

Figure 12. Alteration between the layers of stromatoporoids.

Figure 13. Dolomitic material merged with apex of gastropod.

Figure 14. Altered gastropod after treatment with acids. The dolomitic material is left in relief.

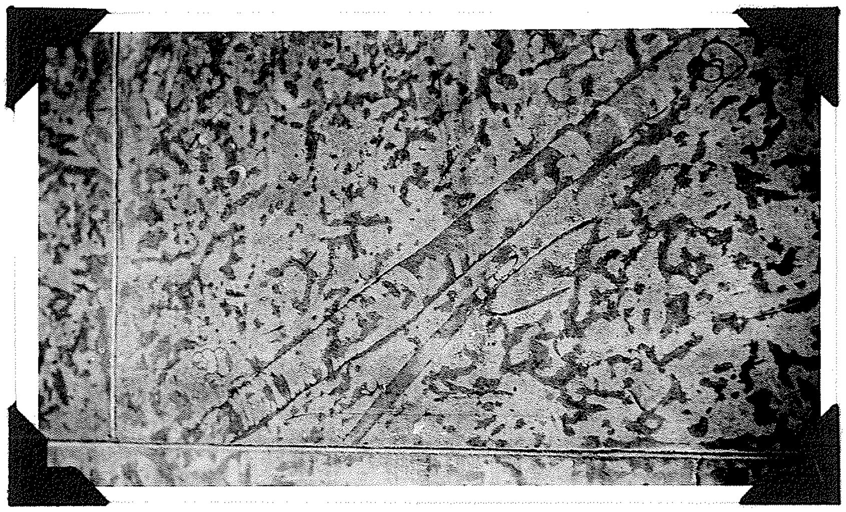

Figure 15. Altered cephalopod.

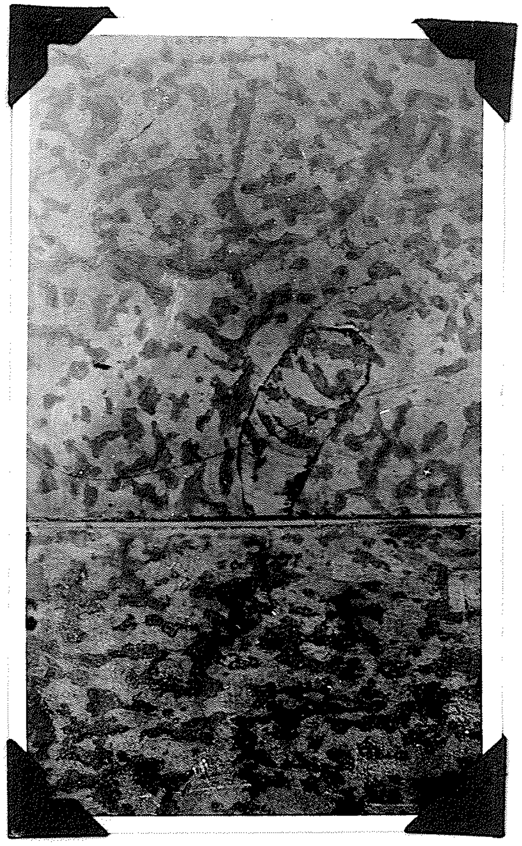

Figure. 16. Altered cephalopod.

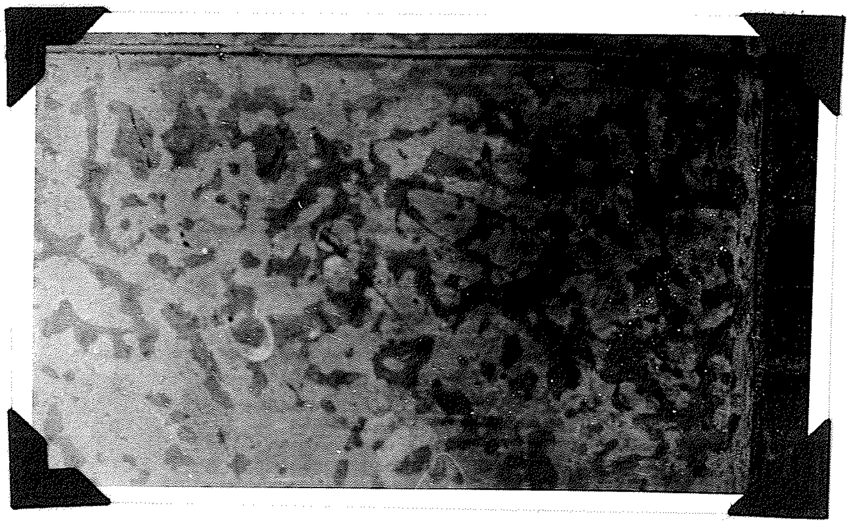

Figure 17. Altered cephalopod.

Figure 18. Chondrites (Buthotrephis) patulus, Whiteaves.

Figure 19. Chondrites (Buthotrephis) cuneatus, Whiteaves.

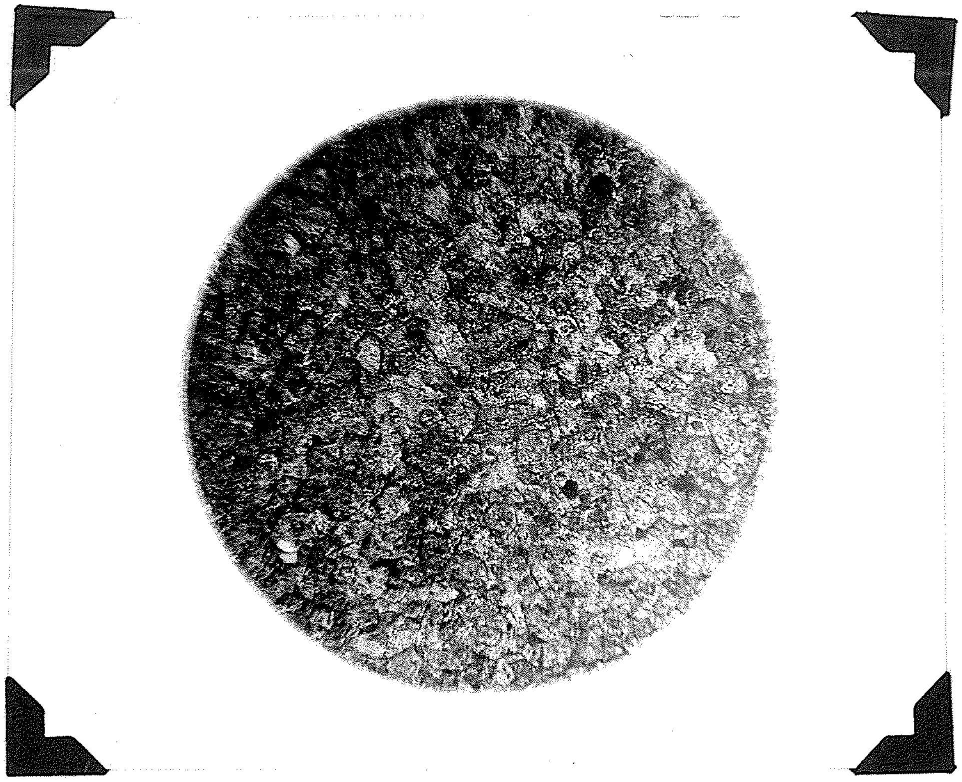

Figure 20. Microphotograph of the Cat Head limestone.

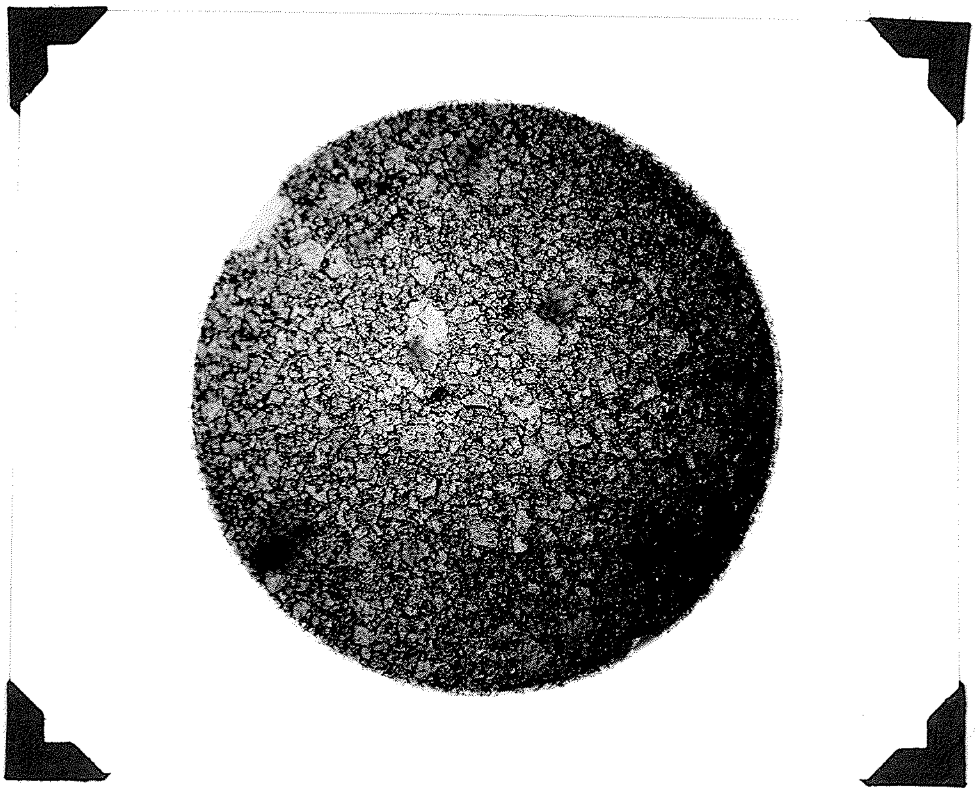

Figure 21. Microphotograph of the light material from the Stony Mountain "lower beds".

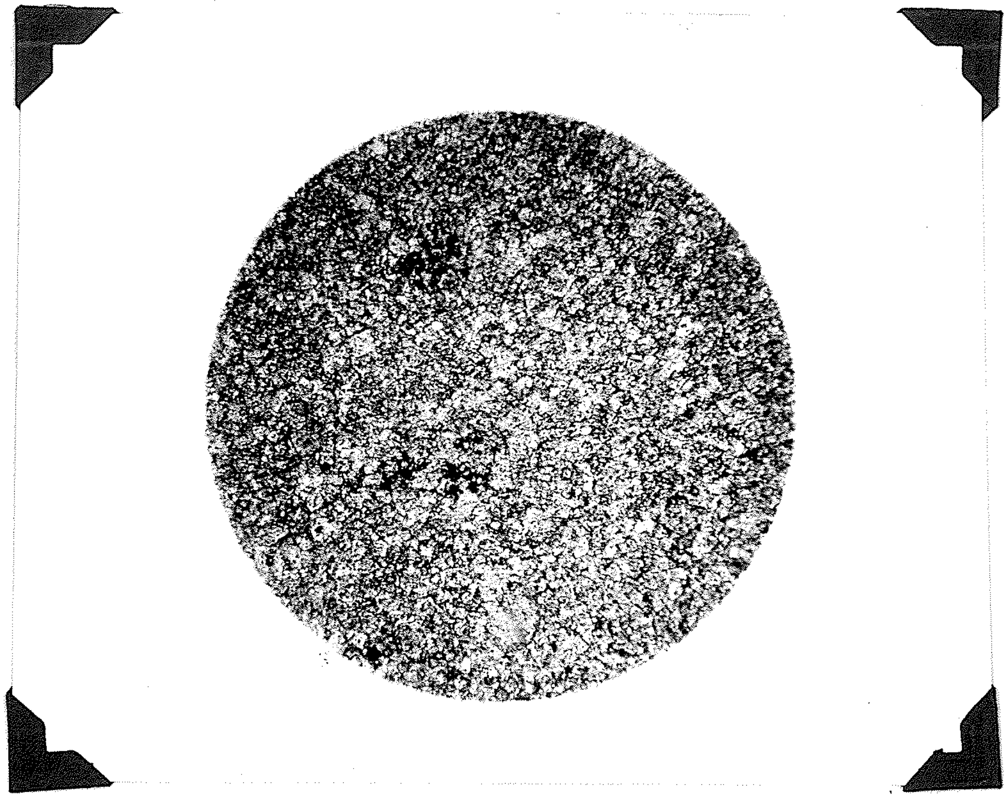

Figure 22. Microphotograph of the dark material from the Stony Mountain "lower beds".

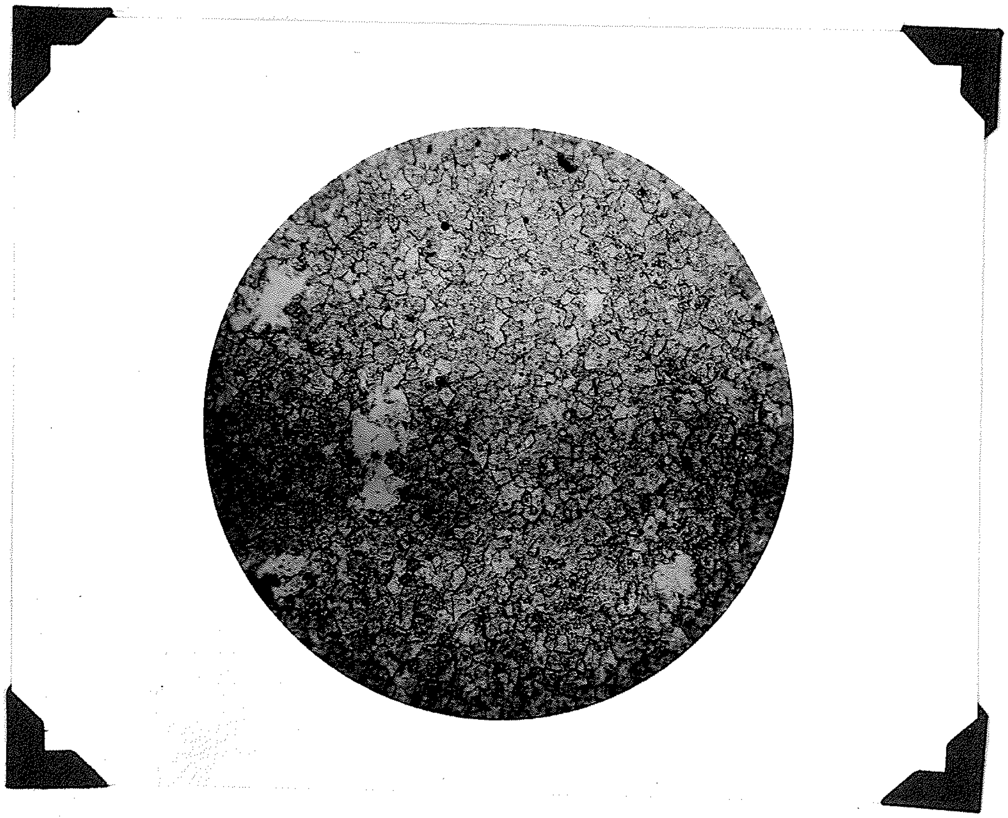

Figure 23. Microphotograph of the light material from the Stony Mountain "upper beds".

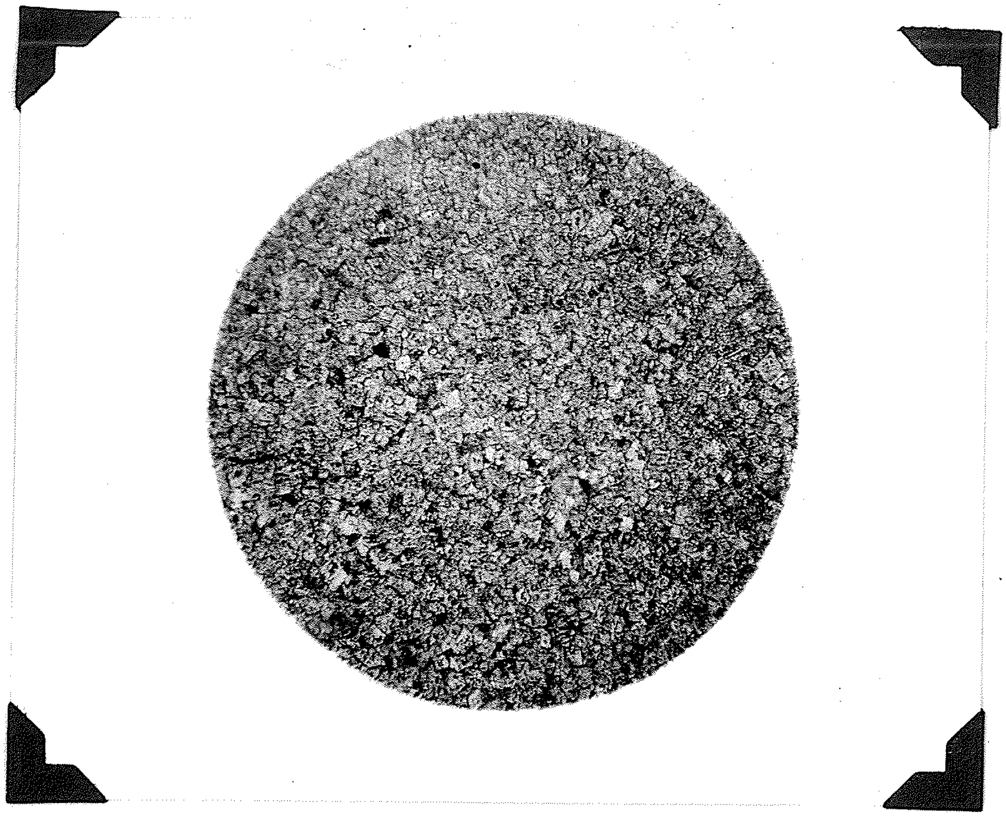

Figure 24. Microphotograph of the dark material from the Stony Mountain "upper beds".

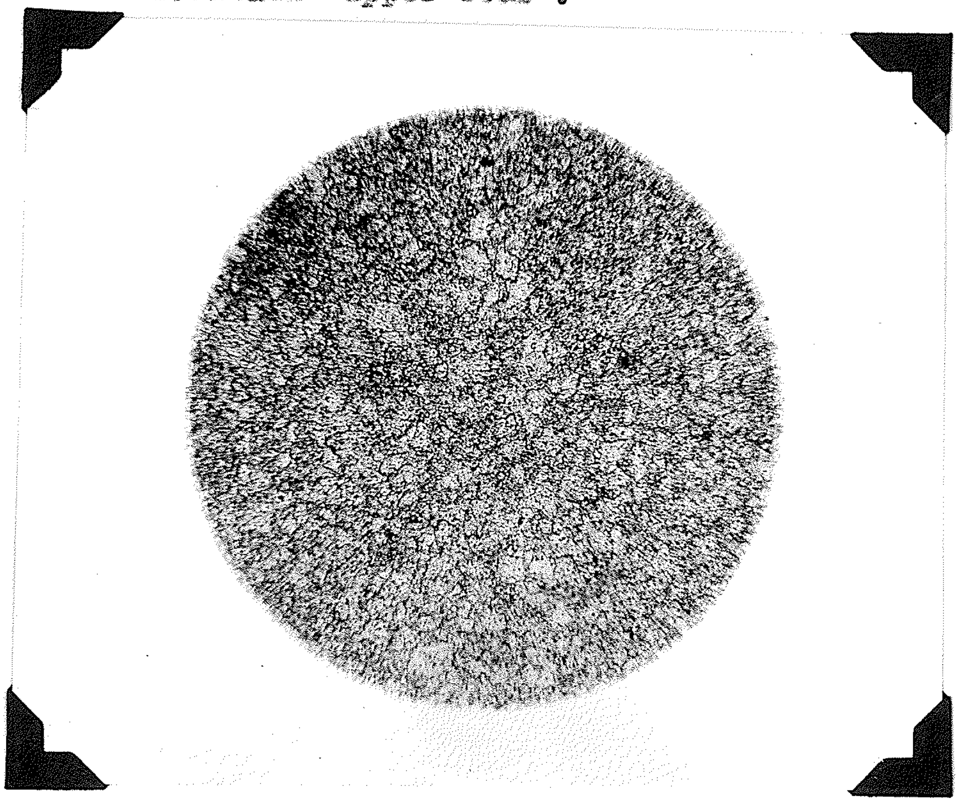

Figure 25. Microphotograph of the *Virgiana decussata* rock.

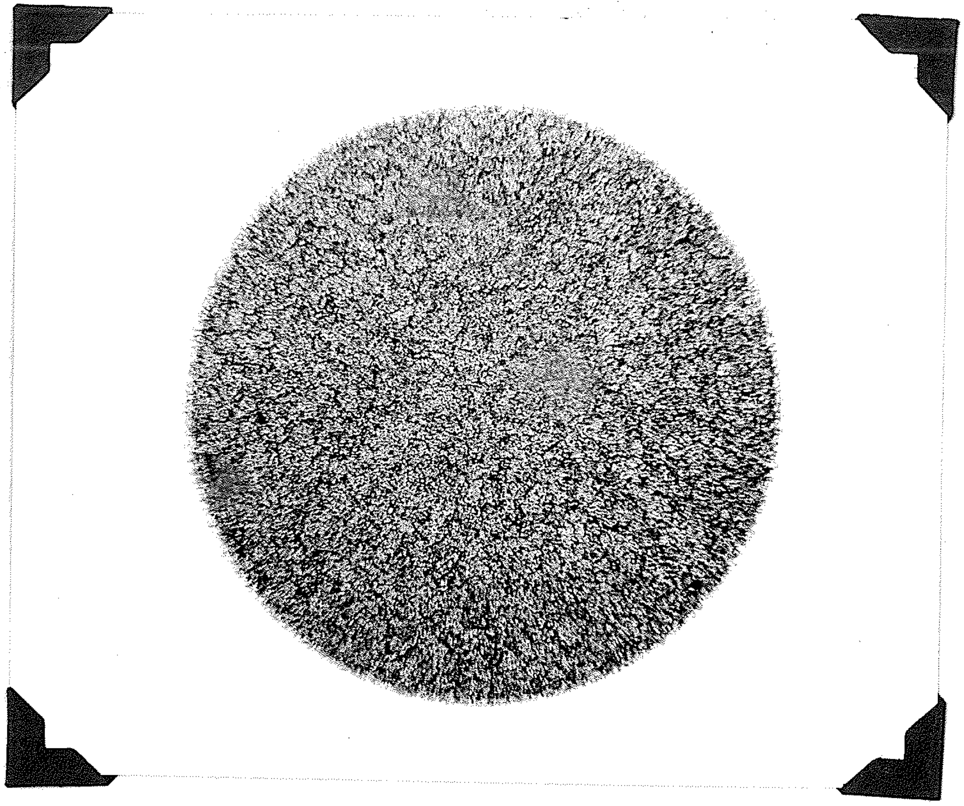

Figure 26. Microphotograph of the Leperditia hisingeri rock.

Figure 27. Mottled Elm Point limestone.

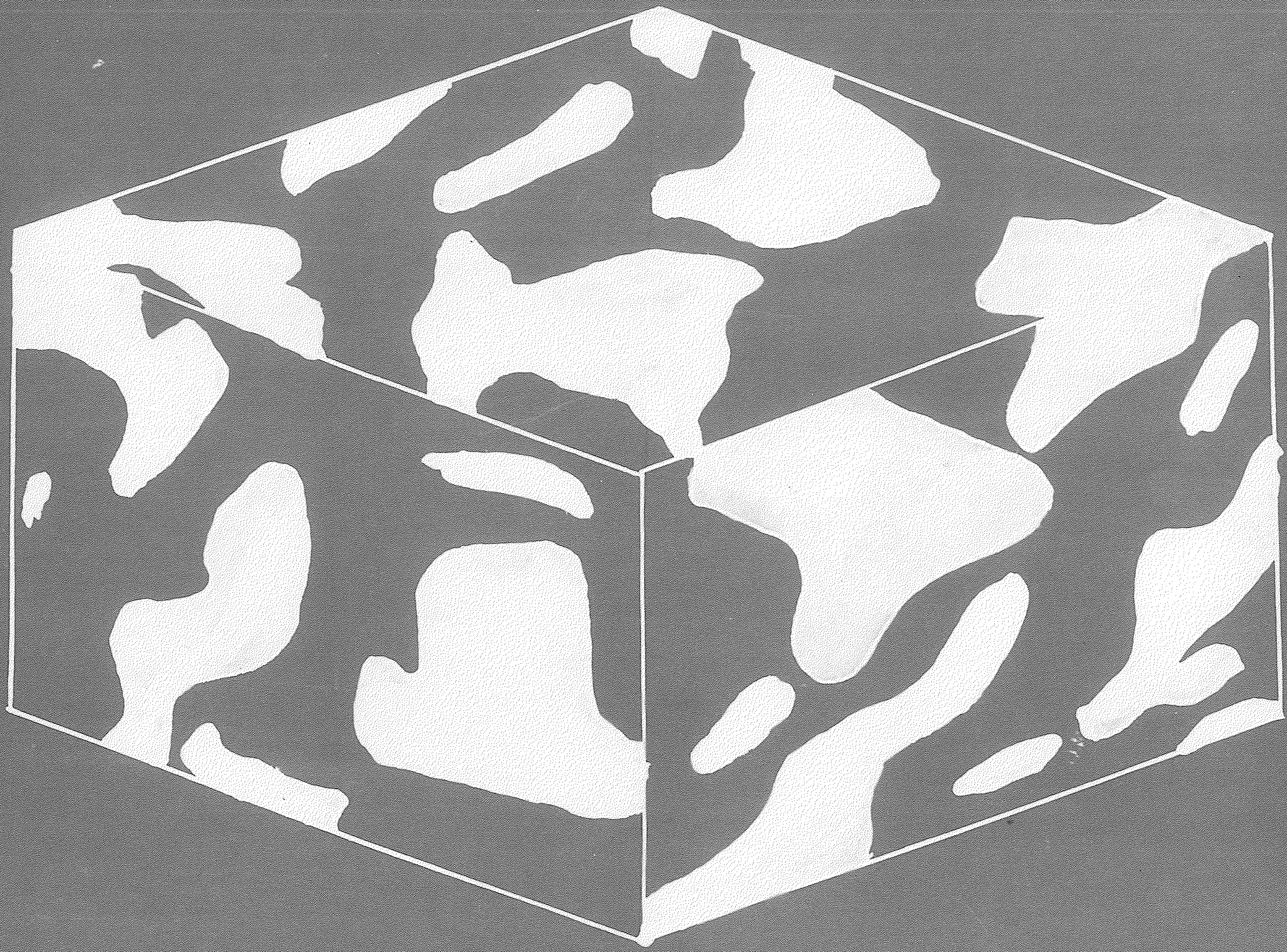

Figure 28.

Figure 29. Light material, Elm Point limestone.

Figure 30. Dark material, Elm Point limestone.

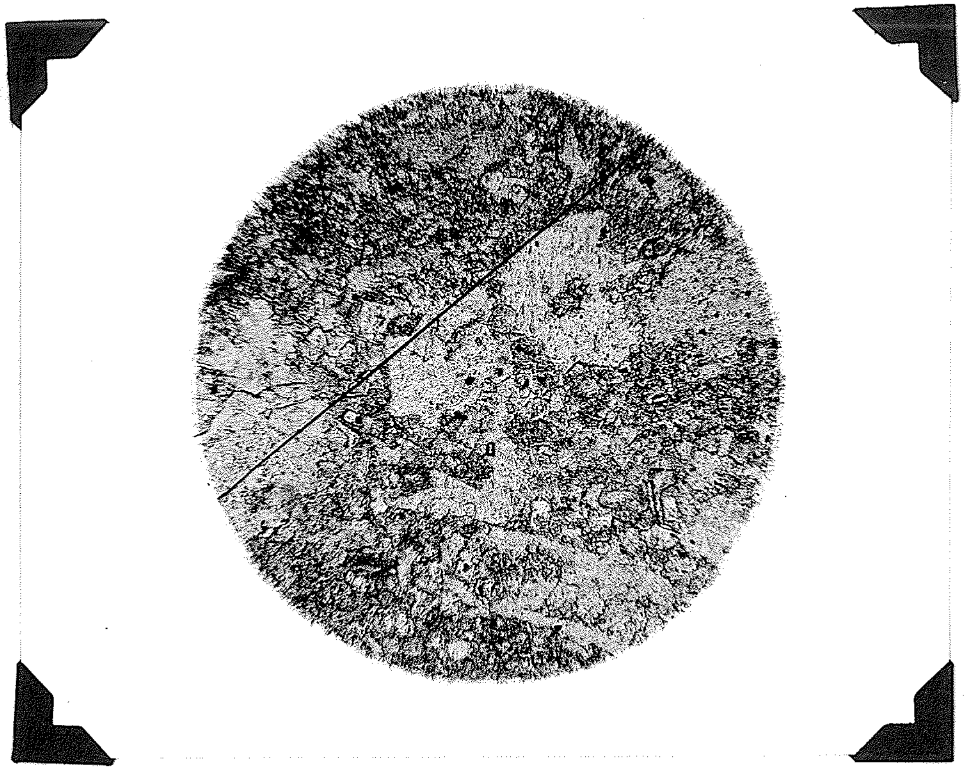

Figure 31. Contact of light and dark material, Elm Point limestone.

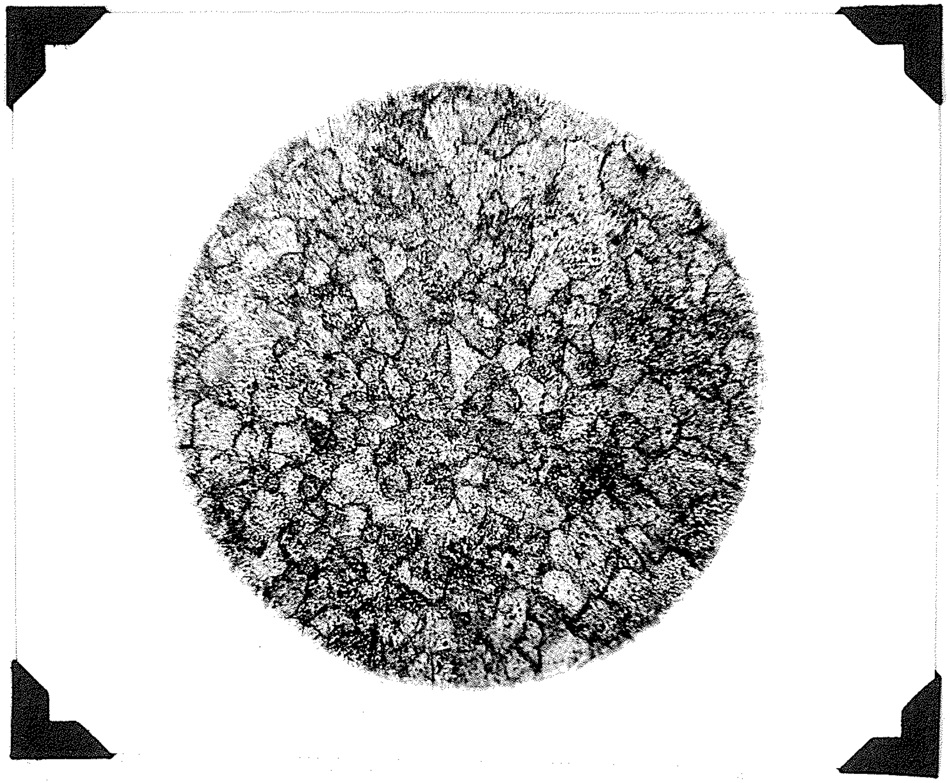

Figure 32. Microphotograph of the Winnipegosan Dolomite.

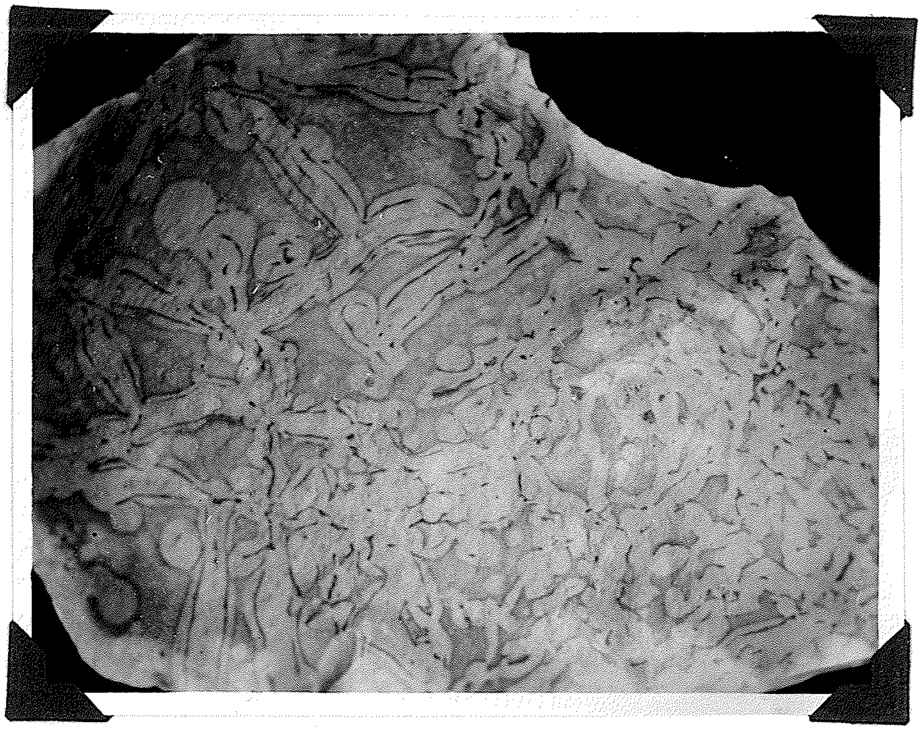

Figure 33. Mottled limestone drift boulder from Gimili, Manitoba.

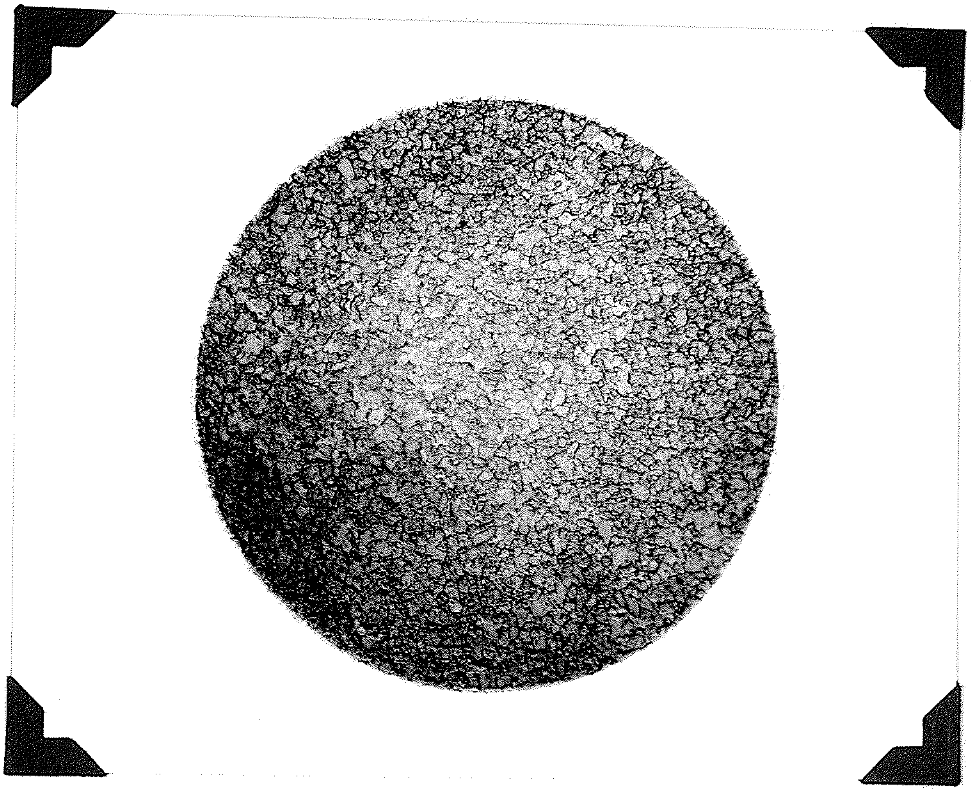

Figure 34. Microphotograph of light material from drift boulder.

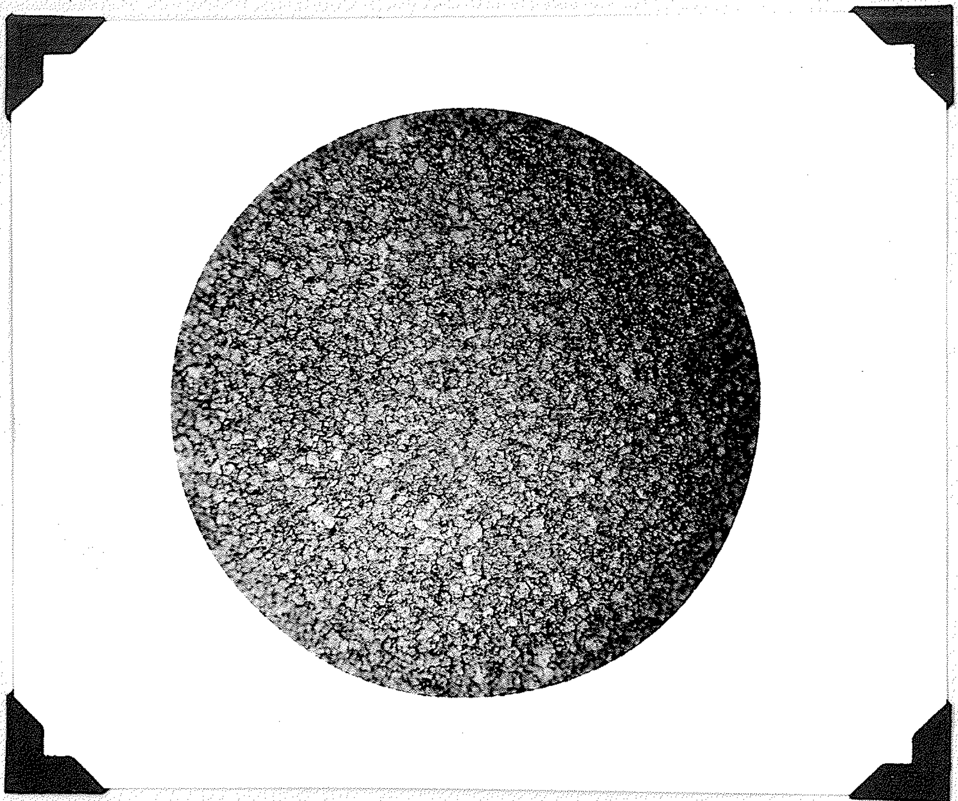

Figure 35. Microphotograph of dark material from drift boulder.