THE ORIGIN OF DOLOMITE

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CONTENTS

THE ORIGIN OF DOLOMITE

Introduction.

Bischof has well said: "No rock has attracted greater attention than dolomite." The problem of the origin of this rock has long occupied the minds of geologists and many theories have been advanced for its formation.

The Tyrol has always been classic ground for dolomite study. As early as 1779, before dolomite as such was recognized as a distinct rock, the Italian geologist, Arduino,[1] called attention to the magnesian limestones which occur in this region in association with rocks of volcanic origin. Two years later Dolimeu[2] remarked upon the peculiar magnesia-bearing limestones of the same region and described some of their properties. But it remained for Saussure[3] in 1792, to make a comprehensive study of the physical and chemical properties of the rock and to give it the specific name "dolomite" in honor of its first describer. Since this time dolomite has been found to have a widespread distribution in both time and space and to constitute one of the most important rocks of the earth's crust. But the mode of formation of the rock has remained from the first a disputed question and in spite of the fact that a voluminous literature has grown up on the subject, the last word has not yet been spoken. It is the purpose of the writer to review the existing theories of the origin of dolomite and to weigh each of these carefully in the light of additional evidence gathered in the course of his investigations.

Field studies were first undertaken in connection with the problem in northeastern Iowa and adjacent parts of Illinois and Wisconsin in 1912, under the auspices of the Iowa Geological Survey, and from this time were carried on privately at intervals in southeastern New York state and New Jersey

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[1] Cited by Morlot, Haidinger's Naturw. Abh., Vol. 1, 1847, p. 305.
[2] Idem., p. 306.
[3] Idem., p. 306.

17

until early in 1914, when a grant from the Esther Herrman Research Fund of the New York Academy of Sciences made possible much more extensive observations during the remainder of that year in Vermont, New York State, Pennsylvania, Ohio, Michigan, Missouri, Illinois and in the province of Ontario. In addition the writer has more recently obtained a large amount of data bearing on the subject in southern Iowa while engaged in a study of the stratigraphy of the Mississippian formations of this region for the State Geological Survey.

OCCURRENCE.

Dolomite frequently occurs as a gangue mineral in ore deposits and commonly forms veinlets and druses in dolomitic limestones. Magnesian spring deposits likewise have been recorded. Vein dolomites formed by the dolomitization of limestone along fissures also are known and several examples of limestones mottled with patches of dolomite in such a way as to give the appearance of a breccia have been described within recent years. It is with the stratified deposits of dolomite, however, that we are chiefly concerned. These are predominantly marine formations, or at least the alteration products of formations originally marine. But fresh-water dolomites also are known. Thus, Leube[4] has described dolomite beds bearing as much as 44.94 per cent of $MgCO_3$ which alternate with less dolomitic and with clayey beds in a Cretaceous fresh-water formation near Ulm in Bavaria, and Knapp[5] has found from 38 to 49.6 per cent of $MgCO_3$ in a fresh-water limestone of the brown coal series at Rödgen near Geissen.

The stratified dolomites may in themselves constitute entire formations ranging up to several hundred feet in thickness, or they may represent only portions of formations, in which case they are interbedded with limestone, sandstone, shale and gypsum. They are widely distributed on the continents and occur in many of the coral islands of the sea.

They range from several shades of gray to buff or yellow in color, and are usually massive and nearly structureless but in

[4]Neues Jahrb. 1840, p. 371.
[5]Jahresber. Chemie. 1847-1848, p. 1298.

places they are thinly and regularly bedded. In fossil content they also exhibit considerable variation. Some dolomites show few or no traces of fossils, while others are highly fossiliferous. In the fossiliferous varieties the fossils in some instances are preserved intact in a silicified condition, but in most cases they are in the form of moulds or casts. Again they vary much in porosity. Some dolomites are very compact, but most of them are vesicular and porous. The size of grain is likewise subject to great variation. The fine-grained, dense varieties are often distinguished from limestone only with difficulty, but the coarser-grained types are more distinct by reason of their tendency to break down into a dolomite sand upon weathering.

With regard to the relation of dolomites to time, they occur in every geological system of the stratigraphic column and are being formed in the seas today. They attain their maximum development, however, in the early Paleozoic systems and roughly decrease in importance with time. This has been demonstrated by Daly,[6] who, by a compilation of a large number of analyses of limestones and dolomites of known age, calculated the ratio of dolomite to limestone in the different geologic periods. (See Table I.)

TABLE I.

Period	No. of Analyses	Ratio of $CaCO_3$ to $MgCO_3$	Ratio of Ca to Mg
Pre-Cambrian:			
(a) From North America except those in (b)	28	1.64:1	2.30:1
(b) From Ontario (Miller)	33	4.92:1	6.89:1
(c) Average of (a) and (b)	61	2.93:1	4.10:1
(d) Best General Average	49	2.58:1	3.61:1
Cambrian (including 17 of the Shenandoah limestone)	30	2.96:1	4.14:1
Ordovician	93	2.72:1	3.81:1
Silurian	208	2.09:1	2.93:1
All pre-Devonian	392	2.39:1	3.35:1
Devonian	106	4.49:1	6.29:1
Carboniferous	238	8.89:1	12.45:1
Cretaceous	77	40.23:1	56.32:1
Tertiary	26	37.92:1	53.09:1
Quaternary and Recent	26	25.00:1	35.00:1
Total	865		

[6]Bull. Geol. Soc. America, Vol. 20, 1909, p. 153.

TABLE

HORIZON	LOCALITY.	CONSTITUENTS				
		CaCO₃	MgCO₃	Al₂O₃ + Fe₂O₃	Insol. Matter	SiO²
Missourian......	Independence, Mo......	97.41	....	0.92	....	1.46
Stones River....	Murat P. O., Va.......	94.88	1.03	1.24	....	2.54
Chambersburg...	Strasburg, Va..........	84.64	1.68	1.48	12.10	....
Beekmantown...	Harrisburg, Pa.........	92.14	3.15	0.06	5.08	....
Wapsipinicon...	Cedar County, Ia.......	93.61	4.20	0.58	1.52	....
Platteville......	Dixon, Ill..............	83.93	5.02	4.44	....	4.78
Elbrook........	Waynesboro, Pa........	83.23	6.03	1.16	8.80	....
Triassic........	Southern Tyrol........	91.50	7.40	...	1.13	....
Kinderhook.....	Marshall County, Ia....	90.04	8.08	0.50	1.22	....
Plattin.........	Cape Girardeau, Mo....	87.23	9.26	0.45	....	2.93
Clinton........	Wilmington, Ohio......	83.77	10.20	2.68	....	2.32
Jurassic........	French Jura...........	82.00	11.22	...	6.88	....
Trenton........	Nat. Gas Belt, Ind.....	83.21	12.48	1.23	2.14	....
St. Louis........	St. Louis, Mo..........	78.97	13.36	0.53	....	2.40
St. Louis........	St. Louis County, Mo..	78.98	14.12	0.99	....	3.39
Wapsipinicon...	Bettendorf, Ia.........	79.60	15.40	0.70	4.46	....
Onondaga......	Bloomville, Ohio.......	62.30	13.18	1.54	....	22.76
Triassic........	Southern Tyrol........	80.50	18.20	...	1.26	....
Beekmantown...	Harrisburg, Pa........	76.10	19.00	1.10	4.70	....
Beekmantown...	Harrisburg, Pa........	76.33	19.88	0.64	2.41	....
Clinton.........	New Jasper, Ohio......	75.27	20.60	2.40	....	2.54
Onondaga.......	Owens Sta., Ohio......	74.00	21.46	1.85	....	1.92
Onondaga.......	Owens Sta., Ohio......	72.85	22.38	2.65	....	1.65
Onondaga.......	Owens Sta., Ohio......	64.00	20.47	2.30	....	12.50
Beekmantown...	Harrisburg, Pa........	64.28	22.32	1.30	11.61	....
Beekmantown...	Harrisburg, Pa........	64.99	23.59	1.57	10.60	....
Onondaga.......	Kelley's Island, Ohio...	71.17	26.82	0.40	....	1.60
Niagara........	Lynchburg, Ohio.......	64.55	25.51	5.18	....	4.88
Clinton.........	Yellow Springs, Ohio...	68.20	28.44	2.40	....	0.72
Niagara........	New Paris, Ohio.......	67.00	29.32	1.32	....	2.50
Beekmantown..	Harrisburg, Pa........	58.53	27.44	2.09	11.90	....
Onondaga.......	Spore, Ohio............	56.04	27.82	3.99	....	8.92
Kinderhook.....	Cooper County, Mo.....	55.54	29.09	2.61	....	11.99
Niagara........	Stone City, Ia.........	63.56	34.76	0.72	0.96	....
Onondaga......	Defiance, Ohio.........	55.30	32.21	1.58	....	11.86
Burlington.....	Ash Grove, Mo.........	61.44	37.68	0.50	....	0.40
Kinderhook....	Sedalia, Mo...........	49.21	31.57	1.08	....	17.69
Wapsipinicon..	Cedar Valley, Ia.......	58.20	39.50	0.90	1.20	....
Cedar Valley....	Bremer County, Ia.....	55.23	39.03	2.12	3.28	....
Beekmantown..	Strasburg Jct., Va.....	51.07	37.80	1.00	10.06	....
Kittatinny.....	Easton, Pa.............	54.40	42.40	2.22	....	1.84
Niagara........	Lannon, Wis..........	52.29	42.27	1.68	....	3.96
Niagara........	Springfield, Ohio.......	53.44	44.49	0.54	....	1.37
Niagara........	New Madison, Ohio....	51.70	45.26	2.70		....
Niagara........	Cedar Valley, Ia.......	51.27	48.09	0.35	0.23	....
Niagara........	Springfield, Ohio.......	46.40	47.53	4.90		....
Niagara........	Greenville, Ohio.......	44.60	50.11	4.60		....
Niagara........	Hillsboro, Ohio	35.57	49.00	2.00	....	13.30

II.

Recalculated on basis of 100% $CaCO_3 + MgCO_3$		AUTHORITY
$CaCO_3$	$MgCO_3$	
100.00	....	Mo. Bur. Geol. and Mines, Vol. 6, 2d ser., p. 235
98.93	1.07	Wm. M. Thornton, Jr., Va. Geol. Survey, Bull. II A, p. 107
98.05	1.95	J. H. Gibboney, Va. Geol. Survey, Bull. II A, p. 60
96.70	3.30	Pa. Sec. Geol. Survey, Rept. M. M., p. 330
95.71	4.29	N. Knight, Ia. Geol. Survey, Vol. 17, p. 531
94.36	5.64	Ill. Geol. Survey, Bull. No. 17, p. 99
93.25	6.75	C. O. Jones, Analysis made for the writer
92.52	7.48	E. W. Skeats, Quart. Jour. Geol. Soc., London, Vol. 61, p. 107
91.76	8.24	G. E. Patrick, Ia. Geol. Survey, Vol. 17, p. 534
90.40	9.60	Mo. Bur. Geol. and Mines, Vol. 6, 2d ser., p. 111
89.14	10.86	S. V. Peppel, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 145
87.96	12.04	F. Pfaff, Neues Jahrb. Beil. Bd. 23, p. 540
86.96	13.04	F. W. Clarke, Bull. U. S. Geol. Survey No. 148, p. 263
85.53	14.47	Mo. Bur. Geol. and Mines, Vol. 6, 2d ser., p. 239
84.83	15.17	Mo. Bur. Geol. and Mines, Vol. 6, 2d ser., p. 237
83.79	16.21	C. E. Ellis, Ia. Geol. Survey, Vol. 17, p. 535
82.54	17.46	S. V. Peppel, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 161
81.56	18.44	E. W. Skeats, Quart. Jour. Geol. Soc. London, Vol. 61, p. 105
80.02	19.98	W. S. Smith, Analysis made for the writer
79.34	20.66	A. S. McCreath, Pa. Sec. Geol. Survey, Rept. M. M., p. 306
78.51	21.49	S. V. Peppel, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 144
77.52	22.48	N. W. Lord, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 163
76.50	23.50	N. W. Lord, Idem, p. 163
75.77	24.23	S. V. Peppel, Idem, p. 161
74.23	25.77	Pa. Sec. Geol. Survey, Rept. M. M., p. 340
73.37	26.63	Idem, p. 331
72.63	27.37	N. W. Lord, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 163
71.67	28.33	S. V. Peppel, Idem, p. 151
70.57	29.43	S. V. Peppel, Idem, p. 145
69.56	30.44	S. V. Peppel, Idem, p. 151
68.08	31.92	Pa. Sec. Geol. Survey, Rept. M. M., p. 330
66.83	33.17	S. V. Peppel, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 163
65.63	34.37	Litton, Mo. Bur. Geol. and Mines, Vol. 6, 2d ser., p. 133
64.65	35.35	A. O. Anderson, Ia. Geol. Survey, Vol. 17, p. 534
63.19	36.81	S. V. Peppel, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 161
61.99	38.01	Mo. Bur. Geol. and Mines, Vol. 6, 2d ser., p. 133
60.92	39.08	Idem, p. 236
59.57	40.43	N. Knight, Ia. Geol. Survey, Vol. 17, p. 531
58.59	41.41	N. Knight, Idem, p. 531
57.47	42.53	J. H. Gibboney, Va. Geol. Survey, Bull. II A, p. 51
56.20	43.80	F. B. Peck, Econ. Geol. Vol. 3, p. 42
55.30	44.70	G. M. Prentiss, Wis. Geol. and Nat. Hist. Survey, Bull. 4, p. 275
54.57	45.43	N. W. Lord, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 151
53.32	46.68	Wormley, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 151
51.60	48.40	N. Knight, Ia. Geol. Survey, Vol. 17, p. 531
49.40	50.60	Wormley, Ohio Geol. Survey, 4th ser., Bull. No. 4, p. 151
47.09	52.91	Wormley, Idem, p. 151
42.06	57.94	Wormley, Idem, p. 153

COMPOSITION.

Normal dolomite, $CaMg(CO_3)_2$, is composed of the carbonates of calcium and magnesium combined in equivalent proportions, and hence consists of 54.35 per cent of $CaCO_3$ and 45.65 of $MgCO_3$. But perfectly pure dolomite is rarely found in nature. Siliceous or argillaceous impurities are commonly present; iron and related metals may replace a portion of the calcium and magnesium; and most important of all, the calcium in many dolomites is far in excess of the normal amount. This, in fact, is true to such a degree in dolomitic limestones that it is often impossible to say where dolomite leaves off and limestone begins, and some confusion has arisen regarding the place where the boundary should be drawn between these two rocks. At present the terms limestone and dolomite are very loosely used, and no attempt is made by many to distinguish between them. Thus, many rocks which are nearly true dolomites are described as limestones by some, while others refer to a rock as dolomite when really it is very low in magnesia; again, still others use the term magnesian limestone freely, regardless of the amount of magnesia present. The attempted classifications of limestone and dolomite show this same uncertainty and lack of regard of the importance of the magnesia content of the rock. For example, Forchhammer[7] concluded that a limestone containing more than 2 per cent of $MgCO_3$ could be called a dolomite. F. W. Pfaff,[8] on the other hand, after a study of a series of analyses of dolomitic limestones, decided that no limestones exist in nature which contain from 7 to 11 per cent of $MgCO_3$, and made this the basis of his classification, calling all magnesia-bearing limestones containing more than 11 per cent of $MgCO_3$ dolomite and all those containing less than 7 per cent of this constituent limestone. A careful examination of a large number of analyses of dolomitic limestones by the writer, however, has proven Pfaff's classification to be untenable, for every gradation has been found to exist in the magnesia content between pure limestone on the one hand and dolomite on the other. (See Table II.) In rare cases the magnesia even exceeds the

[7]Jour. Prakt. Chemie. Vol. 49, 1850, p. 52.
[8]Neues Jahrb., Beil. Bd. 23, 1907, p. 529.

proportion required in normal dolomite, and in these it must be assumed that this excess is due either to the existence of $MgCO_3$ in solid solution or isomorphous mixture in the dolomite or to the presence of free crystals of magnesite.

As to the exact nature of the mixtures of calcite and dolomite in all stages of the transition from limestone to dolomite, little is as yet definitely known. Nor can this be determined except by careful mineralogical studies in conjunction with analytical work or by direct synthetic experiments. It can be safely asserted, however, that calcite and dolomite exist in solid solution or isomorphous mixture to a considerable degree, and that up to a certain point dolomite is miscible with calcite without seriously affecting the latter's mineralogical properties and that again as the composition of dolomite is approached calcite is miscible with dolomite without destroying the latter's individuality. Where the exact transitions take place it is at present impossible to state, but there is some evidence bearing on this point. Thus, Skeats[9] states that in some of the Tyrol limestones $MgCO_3$ is present to the extent of 6 or 7 per cent, without giving rise to any visible dolomite crystals, while a sample of the coral rock from Christmas Island bore over 11 per cent of $MgCO_3$ without showing visible dolomite. Similarly Cullis[10] reports that the coral rock of the Funafuti boring contained as much as 16 per cent of $MgCO_3$ without exhibiting individual crystals of dolomite. It should be noted, however, that this rock had not yet undergone recrystallization. On the other hand, Wallace[11] found that a rock composed of homogeneous crystals but containing only 23.35 per cent of $MgCO_3$ reacted for dolomite optically with Lemberg's solution. Somewhere, then, within the limits of 11, or possibly 16, and 23.35 per cent there appears to be a transition from calcite with dolomite in isomorphous mixture to dolomite with calcite in isomorphous mixture. Whether the transition is sharp or whether there is an intermediate stage in which the dolomite and calcite are present in the form of a mechanical mixture it is impossible to state. It is hoped that future studies will locate this point more accurately,

[9]Quar. Jour. Geol. Soc. London, Vol. 61, 1905, p. 131.
[10]The Atoll of Funafuti: Published by the Royal Society, London, 1904, p. 392.
[11]Congrés Geologique International Compt. Rend. 12th Session, Canada, 1913, p. 875.

for the present confusion attending the classification of the magnesian and dolomitic limestones would then be, in part at least, eliminated. For instance, it might be found convenient to designate all limestones bearing $MgCO_3$ in excess of 3 or 4 per cent and below the limit at which individualized dolomite crystals appear as magnesian limestones, while rocks above this limit which consist wholly or in part of crystals which behave as dolomite but which still contain less $MgCO_3$ than normal dolomite might be designated dolomitic limestones. The more restricted term dolomite could then be applied to those rocks which possess the two carbonates in approximately equivalent proportions. In the present paper no attempt is made to apply any form of classification, and the term dolomite is loosely used for all dolomitic limestones which react microchemically as dolomite, regardless of their exact composition.

HISTORICAL REVIEW.

The theories of the origin of dolomite may be classified conveniently in the following tabular form.

I. Primary deposition theories:
  A. The chemical theory.
  B. The organic theory.
  C. The clastic theory.
II. Alteration theories:
  A. The marine alteration theory.
  B. The groundwater alteration theory.
  C. The pneumatolytic alteration theory.
III. Leaching theories:
  A. The marine leaching theory.
  B. The surface leaching theory.

I. Primary Deposition Theories.

A. The Chemical Theory.—This theory formerly had many followers, and some geologists still adhere to it today. Boné[12] advocated this method of origin as early as 1831, and Bertrand-Geslin[13] was an early supporter of this view. Similarly Wagner,[14] in 1839, favored the view that the dolomites of the French Jura were original deposits rather than alteration products.

[12]Bull. Soc. géol. France, Vol. 1, 1831, p. 115.
[13]Bull. Soc. géol. France, Vol. 6, 1834, p. 8.
[14]Cited by F. Pfaff, Pogg. Annalen, 1851, p. 465.

Coquand,[15] however, concluded that dolomite had a two-fold origin, being in part the product of the action of volcanic agents on limestone, and in part a regular chemical precipitate on the sea bottom. Wissmann[16] almost simultaneously expressed the view that the dolomites of the Tyrol were original deposits, and Petzholdt[17] stated it as his opinion that both the dolomite and the limestone of this region are chemical precipitates, since they grade into each other. This, he believed, would account for the predominance of limestone in the lower part of the section and of dolomite in the upper, since $MgCO_3$ is the more soluble of the two carbonates and would be the last to be thrown out of solution. Fournet[18] likewise interpreted the dolomite of the same region as original.

Forchhammer[19] soon after pointed out that certain dolomitic nodules in the Cretaceous limestones at Faxö were probably chemical. These he believed to be the product of the reaction of the $CaCO_3$ of spring water with the magnesia of sea water. The presence of material resembling travertine in the rocks and other evidences of spring action seemed to lend support to this view.

Delanoue,[20] on the other hand, was inclined to favor the chemical precipitation theory for dolomites in general, regarding secondary dolomites as only local and of little importance.

Liebe[21] in 1855 gave this theory an elaborate setting for the origin of the Zechstein dolomites. To account for these he assumed that the Zechstein sea had been visited by eruptions and violent disturbances through which magnesia was introduced from subterranean sources and the inhabitants of the sea exterminated. Carbon dioxide, possibly contributed by the volcanic action, took the magnesia into solution as $MgCO_3$, which was distributed over wide areas. This then united with the $CaCO_3$ of the sea to form minute crystals of dolomite which after being driven here and there by waves and currents were finally deposited on the sea bottom.

[15]Bull. Soc. géol. France, Vol. 12, 1841, p. 314.
[16]Cited by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 200.
[17]Idem., p. 201.
[18]Bull. Soc. géol. France, 2d. ser. Vol. 6, 1849, p. 502.
[19]Jour. Prakt. Chemie, Vol. 49, 1850, p. 52.
[20]Compt. Rend., Vol. 39, 1854, p. 492.
[21]Zeitschr. Deutsch. geol. Gesell., Vol. 7, 1855, p. 406.

Hunt[22] also expressed himself unequivocally in favor of the chemical precipitation of dolomite, giving it as his opinion that "dolomites, magnesites, and magnesian marls have had their origin in sediments of magnesium carbonate formed by the evaporation of solutions of bicarbonate of magnesia. These solutions have been produced by the action of bicarbonate of calcium on $MgSO_4$; or by the action of bicarbonate of sodium on $MgCl_2$ or $MgSO_4$. The subsequent action of heat has cemented the sediments into magnesite or dolomite."

Cordier,[23] approaching the problem from a philosophical standpoint, was also led to believe dolomites were chemical deposits, and Leymerie[24] entertained similar views. He points out that the dominant salt in the sea today is NaCl, while $MgCl_2$ and $CaCl_2$ are accessory, but supposes that in early Paleozoic time conditions may have been reversed. If then Na_2CO_3 were brought in by rivers or introduced from submarine sources, a double decomposition would set in and dolomite might be deposited. This he believed would account for the constant association of limestone and dolomite both in different beds or layers and in the same bed, and would explain the present high NaCl content of the seas.

Von Rosen[25] about this time claimed chemical precipitation as the probable method of origin of the dolomite and dolomitic limestone of the Düna and Welikaja regions in Finland and Kurland, and Gümbel[26] applied it to the dolomites of the French Jura and of the southern Tyrol. Scheerer,[27] on the other hand, believed that all of the oldest dolomites represent chemical precipitates.

Loretz[28] also favored the view that the dolomites of the southern Tyrol are original formations and leaned towards the chemical theory. The preservation of fine and detailed structures in the rock suggested to him its primary nature.

[22]Am. Jour. Sci., 2d ser., Vol. 28, 1859, p. 382.
[23]Compt. Rend. Vol. 54, 1862, p. 293.
[24]Mémoires de L'Academie Impériale des Sciences de Toulouse, 6th ser., Vol. 2, 1864, p. 307.
[25]Cited by Zirkel, Lehrbuch der Petrographie, 2d ed. Vol. 3, 1894, p. 503.
[26]Cited by Zirkel, Idem, p. 503.
[27]Neues Jahrb., 1866, p. 1.
[28]Zeitschr. Deutsch. geol. Gesell., Vol. 30, 1878, p. 387.

S. F. Emmons,[29] in 1886, adopted the primary theory for the origin of the dolomites of the Leadville district of Colorado. He concluded that the magnesia is an original constituent of these rocks, having been deposited at the same time as the lime. The presence of minute amounts of chlorine in the dolomites as shown by analyses led him to believe that fluid NaCl was included in the dolomite grains when they crystallized.

In still later times Vogt[30] has come out in favor of this view, stating it as his opinion that certain Norwegian dolomites are chemical. The following facts are arrayed in favor of this contention: (1) Although the dolomites are in places of great thickness, they consist in many cases of dolomite of ideal composition; (2) Dolomite layers are interstratified with limestone without transition; (3) Carbonaceous material is wanting in these dolomites; while in limestones derived from organic remains carbonaceous material is always met with.

Ulrich and Schuchert[31] have also implied that certain dolomitic limestones are chemical, as shown by the following statement:

"Except around certain areas composed of pre-Cambrian rocks and supposed to have been islands (Adirondacks and Isle of Wisconsin) where deposits were arenaceous, the upper Cambric sea laid down great beds of limestone. These limestones were chiefly dolomite, and in this case, indicate (1) remoteness from steep shores of the areas receiving them, (2) considerable depth of water, which may explain the unusual paucity of animal remains contained in them, and (3) chemical precipitation as the main source of the material composing them."

The chemical theory has had one of its greatest champions in Suess,[32] who points out that in the Plattenkalk formation beds of dolomite, often containing more than 40 per cent of $MgCO_3$ and of constant thickness and regular contacts, are interbedded with limestone, and maintains that the dolomite was deposited as such from the sea. The following statement is added in a footnote:

[29]Mono. U. S. Geol. Survey, Vol. 12, 1886, p. 276.
[30]Zeitschr. Prakt. Geologie, 1898, p. 4.
[31]New York State Museum, Bull. 52, 1901, p. 633.
[32]The Face of the Earth, English translation, Vol. 2, 1906, p. 262.

"Gümbel has always maintained this view; the dolomitic in-
tercalations in the Potsdam sandstone, the Waterlime of the
upper Silurian of North America, the dolomitic beds of the
upper Devonian of Russia, those which represent the Zechstein
in England and those in the German Keuper, all of them more
or less littoral deposits, are so many examples of the direct
deposition of dolomite."

The chemical theory, however, has been elaborated most fully
by Daly in two very suggestive papers. In the earlier paper[33]
this writer points out that in pre-Cambrian time when the scaven-
ger system of the ocean was not yet developed, the seas must
have been depleted in lime and magnesia due to the precipitating
effect of $(NH_4)_2CO_3$ generated from decaying organisms on the
sea bottom. "The magnesium carbonate should have been most
abundantly thrown down in pre-Cambrian time; its precipitation
must have been lessened through Paleozoic and Mesozoic time
and has reached its minimum since the abyssess of the ocean be-
came abundantly tenanted with scavengers."

In Daly's second paper[34] this theory is developed still further.
A study of nearly 900 representative analyses of limestones dis-
tributed among all the geological periods ranging from the pre-
Cambrian to the recent showed that the ratio of calcium to mag-
nesium is fairly constant for all the pre-Devonian periods, but
that the ratio rises abruptly in the Devonian and continues to
rise to the Cretaceous, where the maximum is reached. (See
Table I, page 259.)

The average Ca:Mg ratio for the pre-Devonian limestones
(3.35:1) is very close to the ratio of Ca to Mg in the rivers
now draining the pre-Cambrian terranes as shown by analysis
of the water of the Ottawa river at Ottawa. "This comparison
of itself suggests that during the pre-Devonian time the river-
borne magnesium and calcium were wholly precipitated after
diffusing to the sea bottom. In fact the correspondence must be
regarded as giving powerful support to the hypothesis." It is
suggested that the marked rise in the Ca:Mg ratio in Devonian

[33]Am. Jour. Sci. 4th ser., Vol. 23, 1907, p. 93.
[34]Bull. Geol. Soc. America, Vol. 20, 1909, p. 153.

and later time may be due to the development of the scavenging fishes, which would prevent organic decay and the consequent generation of $(NH_4)_2CO_3$.

To Daly the fine and monotonous grain of the pre-Ordovician limestones and dolomites means that they are neither of clastic nor of organic origin. For example, microscopic examination of samples of 7000 feet of pre-Cambrian strata exposed in the Forty-ninth Parallel section of the Rocky Mountian geosyncline showed that "the constituent particles are either idomorphic and roughly rhombohedral, or anhedral and faintly interlocking. The former are everywhere of nearly uniform average diameter, ranging from .01 millimeter to .03 millimeter with an average of about .02 millimeter. The anhedral grains range from .005 millimeter to .03 millimeter, averaging about .015 millimeter." The same uniform grain was found to prevail in the Archean dolomites at the head of Priest river, Idaho, in the Belt series of the Clarke Range and in the Siyeh and Sheppard siliceous limestones of Middle Cambrian age of Northwestern Montana. The fact that the average diameters of these carbonate granules are of the same order as the average diameter of calcite and dolomite crystals known to have been formed by chemical precipitation seems to him to be significant.

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

Following closely upon Daly came Linck[35] as an advocate of the chemical precipitation theory. Basing his conclusions upon the conditions of his experimental production of dolomite, he also assumed that $(NH_4)_2CO_3$ derived from the decay of marine organisms was a competent precipitating agent.

The latest investigator to express himself favorably to the chemical hypothesis is Weigelin,[36] who applies it to the dolomites associated with salt and gypsum in the Lower Keuper of West

[35]Monatsh. Deutsch. geol. Gesell., 1909, p. 230.
[36]Neues Jahrb., Eell. Bd. 35, 1913, p. 628.

Württemberg. The upward succession of dolomite, gypsum and salt here suggests to him that all these are the products of evaporating seas.

B. The Organic Theory.—The opinion formerly prevailed in some quarters that organisms have played an important role in the production of dolomite, and recent work has tended to revive this view somewhat.

Forchhammer[37] showed by a series of analyses as early as 1850 that the calcareous skeletons of some organisms contained considerable magnesia.   In the Brachiopods he found the $MgCO_3$ to be uniformly low, not exceeding one per cent, but *Isis hippuris* yielded 6.36 per cent; *Corallium nobile* 2.13 per cent; Serpula sp. from the Mediterranean 7.64 per cent; and *Serpula triquetra* from the North Sea 4.45 per cent. Upon the strength of these results this writer concluded that such magnesia-secreting organisms might build a dolomitic limestone directly.

The chemical studies of Damour[38] also led him to support this theory. Analysis of calcareous algae ("corals") by him showed a high $MgCO_3$ content in four out of six specimens. He records a maximum of 16.99 per cent of this constituent in *Amphiroa tribulus* Lam., while Melobesia sp. nov. yielded 12.32 per cent. Damour concludes, therefore, from the development such forms take on along the shore and on the sea bottom that deposits of magnesian limestone are being formed by them today and must have been formed by them in the past.

Ludwig and Theobold[39] have also emphasized the importance of algae in the deposition of limestone and dolomite. In the travertine of the mineral spring at Nauheim, in the Wetterau, which is deposited through the agency of algae, these writers found a magnesia content ranging up to 11.69 per cent. They are led to venture the suggestion, then, that similar plants may have played an important role in the deposition of older compact limestones poor in organic remains, and perhaps also of much dolomite.

The observations of Doelter and Hoernes,[40] who held that many weakly dolomitic limestones were deposited directly in

[37]Jour. Prakt. Chemie, Vol. 49, 1850, p. 52.
[38]Annales Chim. Phys., 3d ser., Vol. 32, 1851, p. 362.
[39]Pogg. Annalen, Vol. 87, 1852, p. 91.
[40]Jahrb. K.-k. geol. Reichsanstalt, Vol. 25, 1875, p. 293.

the sea through the activity of organisms, are also in accord with the organic theory. Much more recently Nichols[41] has sought to demonstrate the importance of organisms in dolomite formation. Thus, upon analyzing a calcareous nodule taken from the Argus Bank of the Atlantic Ocean at a depth of 28 to 30 fathoms he found a much higher $MgCO_3$ content in the outer portion of the nodule than in its inner portion, the percentages being 10.70 and 4.98 respectively. This anomaly is accounted for on the assumption that "the more highly magnesian corals, serpulae and algae of which the nodule is composed are in the central part diluted by the less magnesian gastropod material. It is probable that the magnesium of the outer part is also somewhat increased by the re-solution of the skeletal material which is always taking place." Nichols then raises the question whether the more ancient organisms may not have secreted even more highly magnesian skeletons, thus:

"If under present conditions corals, etc., secrete skeletons which may contain over ten per cent of magnesia, may they not, under Paleozoic conditions, when, as is usually conceded, the sea water was very different in composition and possibly far more corrosive than at present, have protected themselves by secreting relatively insoluble dolomite skeletons?"

As regards the origin of the nodules, it should be pointed out that Phillipi[42] dissents from the interpretation above given, holding that the higher magnesia content in their outer portion is rather to be accounted for upon the basis of recent dolomitization by magnesia which has been introduced from the sea.

Late investigations by Wallace[43] have tended to lend weight to this theory, since he believes that the occurrence of dolomitic fucoid-like markings in the Ordovician limestones of Manitoba is best accounted for on the assumption that algae bearing considerable magnesia were imbedded in the rock at the time it was deposited and that this magnesia was influential in producing local dolomitization of the limestone.

C. The Clastic Theory.—That some dolomites may represent ordinary mechanical sediments derived from the erosion of older

[41]Field Columbian Museum, Geol. series, Vol. 3, 1906, p. 40.
[42]Neues Jahrb., Festband, 1907, Vol. I, p. 397.
[43]Jour. Geol., Vol. 21, 1913, p. 402.

dolomitic limestones, seems to have been conceived first by Lesley, in 1879,[44] who suggested this mode of origin for an interbedded series of limestones and dolomites of the "Calciferous," exposed in the old Walton quarry, in the west bank of the Susquehanna river, opposite Harrisburg, Pennsylvania. Here "a consecutive series of the beds, all conformable, and all dipping regularly about 30° to the southward afforded a good opportunity for collecting two sets of specimens for analysis, one at the bottom and one at the top of the cut." In all 115 distinct beds with an aggregate thickness of 371 feet were carefully measured and separately sampled both at the bottom and at the top of the opening. The analyses were then carried out in the Survey laboratory at Harrisburg. On the whole, each bed in itself showed remarkable uniformity in composition; but when compared with the associated layers, striking differences were noted. This is well illustrated by the accompanying table compiled from Lesley's report.

TABLE III.

NUMBER OF BED	THICKNESS		$CaCO_3$		$MgCO_3$		INSOLUBLE	
	Feet	Inches	Bottom	Top	Bottom	Top	Bottom	Top
			Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
46	3	6	97.2	90.6	1.7	7.6	0.7	1.8
47	0	10	63.4	68.2	29.5	27.1	6.4	3.6
48	0	5	94.3	95.3	1.9	2.2	3.5	2.2
49	0	2	57.8	66.2	33.2	26.9	8.0	5.7
50	0	6	60.4	62.0	32.1	31.7	5.3	5.1
51	1	11	92.6	95.7	3.2	2.9	3.0	1.7
52	4	0	61.4	68.9	31.9	23.7	5.3	7.2
53	0	5	81.1	88.7	10.0	7.0	4.7	3.4
54	5	2	98.2	97.9	1.3	1.2	1.2	0.7
55	0	11	79.8	79.5	10.8	13.4	8.6	6.9
56	1	0	66.9	66.0	24.2	23.2	7.4	9.7
57	1	10	91.6	91.0	2.4	2.3	5.9	6.8
58	2	0	64.8	60.1	27.4	29.9	7.2	8.6
59	1	10	97.1	99.3	1.8	1.3	1.1	0.2
60	0	10	75.1	76.3	20.9	19.9	3.1	2.4
61	2	4	89.3	95.1	1.5	1.8	8.9	2.1

In a few instances, however, notable variations in the $MgCO_3$ content were found in the same layer. These are indicated in the table below.

[44] Pa. Second Geol. Survey, Rept. M. M., 1879, p. 311.

TABLE IV.

NUMBER OF BED	THICKNESS		CaCO₃		MgCO₃		INSOLUBLE	
	Feet	Inches	Bottom	Top	Bottom	Top	Bottom	Top
			Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
14	12	8	95.85	83.70	2.40	11.85	1.80	3.40
17	2	8	96.60	60.20	1.10	33.40	1.10	5.90
68	14	10	85.1	96.00	10.40	2.30	3.20	1.90

Some of Lesley's conclusions are quoted in full:

Sometimes a bed of limestone only 5 or 6 inches thick crosses the exposure between two equally thin beds of dolomite, yet there is no appearance of gradation in the deposits, nor in their chemical composition. The same percentages of carbonate of magnesia are found at both extremities of the exposure.

In a few cases there is a decided difference in the amount of magnesia at one or other end of the exposure; but whether this be due to some error in the investigation or to a radical change of composition along the bed which exhibits it, is not certain.

There are thick masses of limestone strata with comparatively thin magnesian layers in their midst; and vice versa, there is sometimes a considerable thickness of magnesian rock parted by thin layers of nearly pure limestone.

There are a few layers of an intermediate species; but these are not numerous enough to destroy the remarkable and sudden contrasts of alternate layers of limestone with 2 or 3 per cent of magnesia and layers with 25, 30, 35 or more per cent. In fact the extreme limits are often directly and repeatedly in contact with each other.

The largest percentage of silicate of alumina is almost invariably found in the high magnesian layers.

The only generalization I can make from the above data is a negative one, namely: that no theory of percolation can account for the facts; that no theory of more rapid dissolution of carbonate of lime leaving a growing charge of magnesia behind, will apply to rocks which are neither honeycombed or visibly porous, nor unusually cleft, nor otherwise disturbed; and that any theory to account for the presence of magnesia must treat the layers of both species as equally mechanical sediments; especially, seeing that the larger part of the insoluble matter resides in those which contain most magnesia; while magnesia is present in all of both kinds.

18

Such a theory of origin is favored also by Phillipi[45] to account for certain impure dolomites associated with clastic sediments in the Muschelkalk of Germany. He believes that the material constituting these dolomites probably was derived from the residuum of a limestone originally low in magnesia. This view has been adopted lately by Grabau[46] also, who holds that the upper Silurian waterlimes and certain dolomitic intercalations in the Salina are clastic deposits derived from the erosion of older limestones. The same writer[47] is of the opinion that certain interstratifications of limestone and dolomite likewise are explainable upon the basis of the clastic theory, remarking that the relationship is most satisfactorily explained as a primary difference in the materials deposited, that both the limestone and the dolomite are clastic but are derived from different sources, or that the limestone is organic and the dolomite clastic.

II. Alteration Theories.

A. The Marine Alteration Theory.—The theory that dolomite has had its origin in the alteration of limestone before it emerged from the sea has had many followers and probably is most widely held today. Among the supporters of this view there has been almost unanimous agreement that the sea-water contributed the magnesia, and the only exception to this is the view of Favre[48] who, basing his suppositions upon the conditions of the experimental production of dolomite by Marignac, concluded that the dolomites of the Tyrol were formed in part at least by the alteration of limestone at a temperature of 200° C., and at a pressure of fifteen atmospheres, corresponding to a depth of 150 to 200 meters, by magnesium compounds furnished by the action of sulphurous and hydrochloric acids of volcanic origin on the lava of submarine melaphyr eruptions.

The conception that the alteration might be effected by the magnesia of sea water was first suggested by Dana[49] in 1843, to account for the dolomitic reef rock of the coral islands of the

[45]Frech's Lethaea Geognostica, Vol. 2, 1908, p. 31.
[46]Bull. Geol. Soc. America, Vol. 24, 1913, p. 399.
[47]Principles of Stratigraphy, 1913, p. 760.
[48]Compt. Rend., Vol. 28, 1879, p. 364.
[49]Am. Jour. Sci., Vol. 45, 1843, p. 120.

Pacific. He hinted at this time that the rock might have been formed by the introduction of magnesia through the medium of heated sea water which possibly contained a larger supply of this element than usual. Three years later[50] in discussing the origin of a dolomitic coral limestone from the Island of Metia which contained 38.07 per cent of $MgCO_3$ he says:

"We cannot account for this supply of magnesia except by referring to the magnesian salts of the ocean. It is an instance of dolomitization during the consolidation of the rock beneath sea water, and throws light upon this much vexed question."

In 1872, the same writer[51] expressed the view that the same dolomite had been formed in sea water at ordinary temperatures but perhaps in a contracting lagoon where magnesian and other salts were in a concentrated state. In the latest edition of Dana's Manual[52] this same idea is elaborated without modification, the opinion being held that the concentrated brines in the lagoon would contain $MgCl_2$ and $MgSO_4$ in a state favorable to the formation of dolomite. He then goes on to say that "if this is the true theory of dolomite-making, then great shallow areas or basins of salt-pan character must have existed in past time over various parts of the continental area and have been a result of the oscillation of the water level. Such magnesian limestones contain few fossils, partly because of fine trituration, and partly, no doubt, because of the unusually briny condition of the waters. The frequent alternation of calcite and dolomite strata would indicate alternations between the clear water and salt-pan conditions."

F. Pfaff[53] likewise regarded the marine alteration theory as the most practicable for the origin of the dolomites of the French Jura. He pointed out that the relation of the limestone to dolomite in this formation and the great variation in the composition of the rock was such as to make Wagner's application of the chemical theory to this rock untenable. He further contended that the rock could not have been produced by the action of $MgSO_4$ or $MgCl_2$ on limestone, since no trace of gyp-

[50]Am. Jour. Sci., 2d ser., Vol. 14, 1852, p. 82.
[51]Corals and Coral Islands, 1872, p. 356.
[52]Manual of Geology, 4th ed., 1895, p. 134.
[53]Pogg. Annalen, 1851, p. 465.

sum or of $CaCl_2$ now appear as reaction products in the dolomite. He, therefore, concluded that the most plausible agent of alteration was $MgCO_3$, and that the transformation must have taken place beneath the sea subsequent to the deposition of the limestone as evidenced by the decrease in the magnesia content downwards in the limestone and by the wavy boundary between the dolomite above and the limestone below in the Wisent Valley near Muggendorf.

Sorby[54] expressed himself in favor of the marine alteration theory in 1856, when he suggested that the formation of certain dolomites was effected by the alteration of limestone through the agency of soluble magnesian salts of the sea water "under some peculiar conditions not yet clearly explained during the period when it became so far concentrated that rock salt was frequently deposited; and that the calcareous salt removed during the change had, by decomposition with the sulphates of the sea water, given rise to the accumulation of gypsum. In support of this is an important fact, that some very solid dolomite does even now still contain about one-fifth per cent of salts soluble in water, consisting of the chlorides of sodium, magnesium, potassium and calcium and sulphate of lime, doubtless retained in the minute fluid cavities, seen with the microscope to exist in great numbers. These, like those in most crystals formed from solution, must have been produced at the same time as the dolomite, and caught in some of the solution then present, which is thus indicated to have been of a briny character.

A process the very reverse of that just described is now taking place by the action of dissolved gypsum, by which sulphate of magnesia, frequently efflorescing on the surface of the rock, and carbonate of lime are produced, and this may perhaps in some cases explain why the upper beds of the Permian limestone are now more calcareous than the lower."

Similarly Von Richthofen[55] adopted this theory, in 1860, to explain the formation of the great dolomitic reef rocks of southern Tyrol. He claimed that these dolomite masses represent dolomitized coral reefs formed during a period of subsidence

[54]Rept. Brit. Assoc. Adv. Sci., 1856, p. 77.
[55]Cited by Skeats. Quart. Jour. Geol. Soc. London, Vol. 61, 1905, p. 97.

and that the St. Cassian marly and tufaceous deposits which flank the reefs represent the deposits of lagoons, bays and channels of the coral sea.

Mojsisovics,[56] in his classic memoir on the dolomite reefs of the same region, accepted a theory not essentially different from that of Von Richthofen. He held that the dolomite masses represent altered coral reefs possibly formed in the same manner as the recent one described by Dana, but doubted if the sea which effected the alteration was concentrated in lagoons as postulated by that writer.

Hoppe-Seyler[57] was also a champion of the marine alteration theory. He believed that the magnesia for altering great limestone masses to dolomite could be furnished only by the sea. In like manner, Doelter and Höernes[58] supported this theory in their memoir on dolomite building, attributing the greater part of the dolomites more or less rich in magnesia to the action of magnesia of sea water, especially the $MgCl_2$, on limestone made up of the calcareous skeletons of organisms.

F. W. Pfaff,[59] in 1894, basing his evidence upon the conditions under which he prepared dolomite artificially, concluded that the following chemical compounds are involved in the production of dolomite and magnesite in nature: (1) $CaCO_3$, (2) basic $MgCO_3$, (3) H_2S, (4) NH_3, and (5) $NaCl$. He believed that coral reefs might be altered to dolomite in the following manner: H_2S derived from decaying organisms would react with $CaCO_3$ taken into solution from the reef to form the hydrosulphide of calcium. $(NH_4)_2CO_3$, also resulting from putrefaction, would change a portion of the magnesium salts of the sea to basic $MgCO_3$ which with the H_2S would form the hydrosulphide of magnesium. By the action of CO_2 on the calcium and magnesium hydrosulphides so formed there would be a tendency to form the double carbonate, especially under the concentrated conditions which might result from the drying up of the sea water during ebb movements. Through numerous repetitions of this process a dolomitic reef rock might in time result.

[56]Die Dolomitriffe von Süd Tirol, 1879, p. 505.
[57]Zeitschr. Deutsch geol. Gesell., Vol. 27, 1875, p. 495.
[58]Jahrb. K.-k. geol. Reichsanstalt, Vol. 25, 1875, p. 293.
[59]Neues Jahrb., Beil. Bd. 9, 1894, p. 485.

Later experiments by this author[60] led him to modify this
view, but he did not abandon it completely, still maintaining
that it would apply frequently and that it was especially appli-
cable to the dolomite of the Neckar in Comstalt. In this new
series of experiments Pfaff found that pressure must be re-
garded as an important factor in dolomite formation, since he
obtained the best results in his artificial production of the min-
eral at pressures ranging from forty to sixty atmospheres. He
concluded, therefore, that dolomitization must go on most ef-
fectively at a depth beneath the sea corresponding to this pres-
sure. Thus, ideal conditions for dolomitization should exist in
a sea like the Caspian, which attains a depth of from 180 to 1800
meters and is more or less concentrated. Such conditions, ac-
cording to him, may have obtained when the dolomites of the
Keuper and Haupt were formed; and the dolomite which oc-
curs along with salt and gypsum in the Rauhwacke and Raibler
strata might be explained in the same manner.

The paucity of fossils in some dolomites is attributed by Pfaff
to the fact that the sea may have been in a concentrated state
when they were deposited. He, therefore, believes that dolomiti-
zation takes place contemporaneously with deposition in some
cases and in support of this he cites analyses showing a high
magnesia content in slimes dredged from a considerable depth
in the modern seas. One of these, taken from Pourtales Plateau,
off the coast of Florida at a depth of 150 to 500 meters, bore
12.39 per cent $MgCO_3$ and 47.11 per cent $CaCO_3$, but also was
high in phosphate of lime and in iron. The dolomite of the
French Jura, however, he regards as having been formed by
the alteration of limestone subsequent to its deposition, agree-
ing in this particular with the elder Pfaff. A concentration of
the sea water due to its being shut off from free intercourse with
the open ocean might bring about dolomitization after lime-
stones were formed.

The view that pressure induced by considerable depth is
an important factor in dolomite formation, however, is not
shared by Phillipi,[61] who points out that dolomite is associated

[60]Neues Jahrb., Beil. Bd. 23, 1907, p. 529.
[61]Neues Jahrb., Festband, 1907, Vol. I, p. 397.

with sandy sediments in the Röt and Keuper and that the presence of calcareous algae in the dolomite of the Alpine Trias proves that this could not have been formed in a deep sea as urged by Pfaff, since algae seldom live below 80 fathoms and never so deep as 200 fathoms. Moreover, Phillipi cites evidence of dolomitization at shallow depths and at ordinary concentration in the modern seas. For instance, he believes that the calcareous nodules described by Nichols from the Argus bank, of which one was found to contain 10.70 per cent of $MgCO_3$ in its outer portion, furnish an example of recent dolomitization at a depth not greater than thirty fathoms. Moreover, certain limestone lumps dredged from the Seine bank northeast of Madeira at a depth of about 150 meters were found to bear 11 to 18 per cent of $MgCO_3$. Microscopic study showed the presence of dolomite crystals in the lumps and every stage of the alteration could be traced. In addition to the dolomite crystals scattered through the mass others appear lining cavities in the rock and these are believed to have been deposited chemically. The lumps evidently are not being formed today, because the organisms imbedded in them are not the same as those now living on the Bank, and what is more, their outer surfaces show corrosion effects. But Phillipi believes they were formed in shallow water at ordinary concentration and that they were brought to their present level by subsidence.

The dolomites of the Aspen District of Colorado are best explained upon the basis of the marine alteration theory, according to Spurr,[62] who expresses himself as follows:

"It is probable, therefore, that the Silurian dolomite of the Aspen district was originally deposited in quiet seas, and was built up from calcareous sediments; that these beds were subsequently altered to dolomite by the magnesium salts of a great evaporating shallow inland sea, and that the alteration was accompanied by the production of the crystalline structure characteristic of the rock." The same method of origin is ascribed to the overlying dolomites of the Carboniferous which Emmons had previously regarded as chemical deposits.

[62]Mono. U. S. Geol. Survey, Vol. 31, 1898, p. 12.

Calvin and Bain[63] adopt an analogous explanation for the origin of the Galena dolomite of the upper Mississippi Valley. On page 410 they state that "it looks as if dolomitization had affected the limestone .... after the formation was complete; that the process began at the top and progressed downwards; and that the depth to which the change descended was, in some instances and to some extent at least, determined by the presence or absence of impervious beds of shale." On page 441 their views are elaborated much more fully, thus:

"It has been said that probably the Galena limestone owes its dolomitic character to the fact that, toward the close of the interval represented by the formation named, the area now occupied by the lead-bearing limestone was an isolated, or partly isolated, basin in which the sea waters were concentrated by evaporation. The City of Dubuque is located in what was the central part of this land-locked basin. In order that the concentration necessary to produce dolomitization of the limestones might be possible, it is a fair assumption that the interval was one of arid climate, one in which loss by evaporation exceeded the volume of drainage water received by the basin from adjacent lands."

Van Hise,[64] on the other hand, tends to minimize the importance of dolomitization before the limestones emerge from the sea and emphasizes the importance of ground water as a dolomitizing agent. Observe the following statement:

While it is clear that dolomitization below the sea may locally go far, the usual facts of observation correspond with the conclusion above given, that dolomitization below the sea is usually very partial, and that the Metia example is exceptional..... It is entirely possible that locally the Cambro-Silurian limestone was dolomitized more extensively below the sea than is the case, on the average, for the later limestone formations. Indeed, it has been supposed that this has been deposited in a mediterranean sea, and that the entire sea may have had to some extent the concentrated conditions at Metia described by Dana. But it appears certain to me, even if the dolomitization was further advanced in the case of some of these formations while below the sea than can be paralleled by recent exten-

[63]Iowa Geol. Survey, Vol. X, 1899, pp. 410 and 441.
[64]Mono. U. S. Geol. Survey, Vol. 47, 1904, p. 803.

sive formations, that they have subsequently been much further dolomitized and the magnesium extensively rearranged since the limestones emerged from the sea.

Branner[65] about this time furnished evidence of recent dolomitization through the agency of sea water in an old reef rock of the stone reefs of Brazil. This rock was found to bear 12.98 per cent of $MgCO_3$ and the assumption was made that part of the lime of the coral rock had been replaced by magnesium from sea water. The rock is still within reach of sea water, and dolomitization is believed by him to be still in progress. The structure of the rock disappears in proportion as the dolomitization proceeds.

Several examples of altered coral reefs have been described by Skeats[66] from the southern Pacific. Dolomite occurs in several of the elevated coral islands there, but attains its greatest purity in Christmas Island, where it contains as much as 43.3 per cent of $MgCO_3$. This author holds that Dana's theory with some modification probably applies here, and believes that the view that limestone is altered to dolomite at a considerable depth corresponding to a particular pressure is untenable. This is indicated by the fact that in several of the islands the highest rocks are dolomitized and the only movement of which there is evidence since their formation m shallow water is one of elevation. He states that "it seems probable that the introduction of magnesia into the limestone does take place from the waters of the lagoon under certain favorable conditions," but adds that "it is improbable that concentration to any marked extent can take place in lagoons unless they are entirely shut off from the sea." The CO_2 liberated by the decay of the animals and plants of the reef would help to dissolve $CaCO_3$, which might then react with the $MgSO_4$ of sea water to give rise to dolomite, the more soluble product $CaSO_4$ remaining in solution. He concludes that since the extent to which the alteration proceeds must depend upon the duration of the exposure of the limestones to the conditions producing dolomitization, the occurrence of dolomite at several different

[65]Bull. Mus. Comp. Zool., Vol. 44, 1904, p. 264.
[66]Bull. Mus. Comp. Zool., Vol. 42, 1903, p. 53.

horizons in an island might be accounted for upon the basis of changes in the rate of subsidence or elevation.

In a very suggestive paper entitled "On the Chemical and Mineralogical Evidence as to the Origin of the Dolomites of Southern Tyrol"[67] the same writer elaborates his views still further. He emphasizes again that dolomitic coral reefs could not have been formed at great depths, and points out that dolomitization of coral reefs is not confined to concentrated lagoons since the outer parts of fringing reefs facing the open ocean are sometimes dolomitized. Thus, some of the fringing reefs of the Fiji Islands are altered, and the raised fringing reefs along the coast of the Red Sea are also occasionally dolomitic. He believes, therefore, that "the Schlern dolomite originated first as a limestone, composed of organisms, in a slowly subsiding area. Dolomitization of the limestone in superficial waters kept pace with the slow subsidence, so that the whole thickness of 3,000 feet or more of rock was continuously and uninterruptedly converted into dolomite during the Triassic Period." In conclusion Skeats lists the following conditions as favorable to the formation of dolomite masses:

(a) Shallow water between 0 and 150 feet in depth and corresponding to a pressure of 1 to 5 atmospheres.

(b) The presence of carbon-dioxide in comparative abundance, causing the partial solution of the limestones and the possibility of chemical interchange with the magnesium salts in sea water.

(c) Porosity of the limestones, allowing the percolation of sea water through the mass of the rocks.

(d) Sufficiently slow subsidence or elevation to render the change from calcite to dolomite complete.

Other examples of dolomitization believed to have been effected by sea water have been described recently by Dixon[68] as occurring in the Carboniferous limestones of South Wales. In the Main limestone member of the series he finds evidence of two distinct periods of dolomitization. The first of these affects certain horizons of the Mumbles Head and Laminosa divisions over wide areas and is regarded as contemporaneous, while the second

[67]Quart. Jour. Geol. Soc. London, Vol. 61, 1905, p. 97.
[68]The Geology of the South Wales Coal Fields, Part 8: Mem. Geol. Survey, England and Wales, 1907, p. 13.

affected the limestone along fissures and hence is subsequent. The contemporaneous dolomitization produced extensive beds and pockets of dolomite and gave rise to a peculiar mottled rock designated as pseudo-breccia. This alteration is believed by Dixon to have been inaugurated so shortly after deposition that the magnesian salts were derived from the Carboniferous sea itself. He indeed asserts that at one place the alteration must have proceeded during the formation of the limestone. Thus, a conglomerate interbedded with the limestone at Pendine contains fragments of Carboniferous limestone which was dolomitized before it was incorporated in the conglomerate. This contemporaneous dolomitization is believed to have taken place in shallow seas since the limestones affected show evidence of shallow water deposition. The subsequent dolomitization is thought to have taken place much later through the agency of underground water.

Peach and Horne[69] are of the opinion that the Cambrian dolomites of the Northwest Highlands of Scotland were formed by the dolomitization of calcareous sediments on the sea bed itself; but they regard it as possible that there may have been also an enrichment of magnesia through the leaching out of the more soluble calcareous material of a slightly magnesian ooze, possibly made up of the secretions of unicellular plants of the plankton.

The marine alteration theory has been adopted likewise by Salomon[70] in recent years to explain certain nests and tongue-like extensions of dolomite in the Ladinic limestones of the Alps. Similarly Walther[71] recognizes that dolomites may be produced in this manner. Following Nadson, he suggests that the $MgCO_3$ which enters into the dolomite may be deposited through the influence of bacteria of the sea water standing in the pores of the rock.

In favor of some method of alteration capable of operating over wide areas are the observations of Weller[72] also, who, from a comparison of the faunas of the Galena and Niagaran dolomites of the Upper Mississippi Valley with their non-dolomi-

[69]The Geological Structure of the Northwest Highlands of Scotland: Mem. Geol. Survey, Great Britain, 1907, p. 370, ff.
[70]Abh. K.-k. geol. Reichsanstalt, Vol. 21, Part I, 1908, p. 408.
[71]Geschichte der Erde und des Lebens, 1908, p. 90.
[72]Bull. Geol. Soc. America, Vol. 22, 1911, p. 227.

tized equivalents in other regions, concluded that they must have been deposited first as limestone and later metamorphosed.

Blackwelder[73] also advocates this method of origin for the Bighorn dolomite of Wyoming; but the low porosity of the dolomite (1.31 per cent) and its sharp contact with the limestone interbedded with it and underlying it leads him to favor the view that it was not formed by the substitution of magnesium for half the calcium in normal limestone, but that it has resulted from progressive alteration during deposition. Thus:

The remaining fourth suggestion to be examined is that the material of the Bighorn dolomite was originally deposited in the form of lime carbonate growths, shells, or ooze, but was progressively altered to dolomite before actual lithification took place, in consequence of chemical reactions in the basal layer of the sea water in which deposition was proceeding. . . . If, as assumed, this process of converting lime carbonate into dolomite during crystallization took place in the loose sediment lying undisturbed on the ocean floor, there seems to be no reason why it should have affected a layer more than a few inches in depth at any one time. If this view is correct, it helps to explain the alternation of dolomites and limestones in many formations and the fact that the beds underlying the Bighorn formation are pure limestone rather than dolomite.

To this hypothesis of the dolomitizing of lime carbonate deposits in the course of their deposition I find no positive objection, and as it apparently explains most of the observed facts, it seems to me the most promising of the suggestions which have made.

In this particular, then, Blackwelder follows Daly,[74] who believes that the magnesia content of the pre-Devonian limestones is original and that "in many, if not all, cases the dolomite crystals may have been formed at or near the surface of the ancient calcareous muds by the interaction of the magnesium salts of seawater with the more easily precipitated calcium carbonate."

As regards the conditions obtaining when the Bighorn dolomite was formed, Blackwelder states that "experimental work has shown that strong solutions of magnesium salts are deleterious to the growth of animals and plants, but inasmuch as the

[73]Bull. Geol. Soc. America, Vol. 24, 1913, p. 607.
[74]Bull. Geol. Soc. America, Vol. 20, 1909, p. 153.

Bighorn sea evidently contained abundant living organisms—
many of them, like the corals, very delicately adjusted to their
environment—it seems unlikely that the magnesium content could
have been more than two or three times as great as in the pres-
ent ocean.'' He believes that the deposits were laid down in a
warm epicontinental sea less than 100 to 200 meters in depth.

The late views of Nahnsen[75] likewise are in line with the theory
of the alteration of limestone beneath the sea. He describes a
horizontal seam of dolomite with wavy boundaries in the Upper
Jurassic limestone of North Germany, and concludes that the
alteration probably took place beneath the sea before the rock
solidified, since solutions would not circulate freely after recrys-
tallization.

B. The Ground Water Alteration Theory.—That ground
water is capable of accomplishing local dolomitization under
favorable conditions there can be no doubt, and there has been a
tendency on the part of some to believe that this method of
alteration is of far-reaching significance. Most writers who
have supported this view have emphasized the importance of the
$MgCO_3$ of ground water as the dolomitizing agent, but some have
advocated that $MgSO_4$ was very effective. For instance Col-
legno, as early as 1834[76] pointed out the frequent association of
gypsum and dolomite in the St. Gothard region and regarded
these both as transformation products resulting from the action
of the $MgSO_4$ in surface water on limestone. For similar rea-
sons Haidinger[77] advocated this method of origin, but since he
found evidence that under ordinary conditions a solution of
$CaSO_4$ tends to convert dolomite into $MgSO_4$ and $CaCO_3$ he as-
sumed that the contrary change takes place at great depths and
under considerable pressure. In this view Haidinger was close-
ly followed by Morlot.[78]

That dolomite might be formed by the partial replacement of
calcite by magnesium carbonate was first pointed out by Haidin-
ger,[79] who described a dolomite pseudomorph after calcite and in-

[75]Neues Jahrb., Beil. Bd. 35, 1913, p. 277.
[76]Bull. Soc. géol. France, Vol. 6, 1834, p. 106.
[77]Cited by Bischof, Elements of Chemical and Physical Geology, English transla-
tion, 1859, p. 158.
[78]Haidinger's Naturw., Abh. Vol. 1, 1847, p. 305.
[79]Trans. Roy. Soc. Edinburgh, 1827, p. 36.

timated that it had been formed in this manner. It remained for Beaumont,[80] however, to put this theory into definite form. Reasoning on the basis that the replacement was molecular and that one out of every two equivalents of $CaCO_3$ was replaced by $MgCO_3$ he calculated that the transformation of limestone to dolomite should be accompanied by a decrease in volume of the rock to the extent of 12.1 per cent. This, he believed, would explain the cavernous character of the dolomites of the Tyrol. Actual porosity determinations of a sample of dolomite from the Alps by Morlot,[81] who obtained the value of 12.9 per cent, later seemed to confirm this prediction.

Scowler[82] also favored this view for the origin of the Carboniferous dolomites of Ireland, believing that the alteration might readily be accounted for by the infiltration of water charged with $MgCO_3$. He suggested that the magnesia was derived from an igneous or ancient Paleozoic rock, or from springs.

In discussing the dolomite of the coral island of Metia Jackson[83] suggested that ascending spring water bearing $MgCO_3$ might have effected the change. Likewise, Haussmann[84] believed that the dolomite of the Muschelkalk was produced by the action of $MgCO_3$ of ascending thermal springs on limestone.

Nauck[85] also cited an instance where he believed limestone had been transformed to dolomite by $MgCO_3$, and Bischof[86] pointed out that since dolomite pseudomorphs may be formed by the action of $MgCO_3$ on calcite, the substitution might also be expected to take place in amorphous carbonate of lime or in compact limestone. "Consequently dolomite would be produced whenever carbonate of lime in any state is brought into such conditions as are requisite for conversion into double carbonate of lime and magnesia. The essential conditions of this conversion are the permeation of carbonate of lime by water containing bicarbonate of magnesia, which is one of the most common constituents of spring water."

[80]Bull. Soc. géol. France, 1836, p. 174.
[81]Compt. Rend., Vol. 26, 1848, p. 311.
[82]Jour. Geol. Soc. Dublin, Vol. I, 1838, p. 382.
[83]Am. Jour. Sci., Vol. 45, 1843, p. 140.
[84]Neues Jahrb., 1854, p. 478.
[85]Pogg. Annalen, Vol. 75, 1848, p. 129.
[86]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 166.

It will be observed that most of the foregoing advocates of the ground water alteration theory attributed the source of the magnesia to spring water. An entirely different idea, however, was entertained by Green[87] who, in 1876, suggested that the $MgCO_3$ might be furnished by the decomposition of olivene sand incorporated in the limestone at the time it was formed. He refers to the fact that in the Hawaiian Islands olivene forms the main component of the sand of the seashore wherever the sea meets the lava and that fine olivene sand is frequently mixed with the coral sand and even impregnates the coral rock. He suggests that the silica of the olivene sand so imbedded in limestone might be removed in solution and the magnesia converted into $MgCO_3$, which would then give rise to dolomitization. It is his belief that many magnesian limestones and dolomites as well as serpentinous streaks in limestone may have been formed in this manner.

There always has been a tendency to regard dolomite veins in limestone as the product of the reaction of the $MgCO_3$ of circulating ground waters on limestone. For instance Schmidt[88] expressed the view, in 1875, that the dolomitized limestone associated with the ores of the Joplin district was formed in this way. In like manner Michael[89] attributes the dolomitization of the Muschelkalk along lines of disturbance at Tarnowitz, in southeastern Prussia, to the same cause. The dolomitization there appears to be closely bound up with the mineralization phenomena, the sulphide ore deposits being limited to the dolomitic areas.

The local dolomitization effects in the Leadville limestone of the Aspen district of Colorado[90] also are attributed to the action of the magnesia of ground water by Spurr. The limestone is dolomitized along faults and fractures and "the local dolomitization almost invariably accompanies the ore." No tangible evidence as to the conditions under which these vein dolomites were formed could be obtained in the Aspen district, but at Glenwood Springs, Colorado, only forty miles away, Spurr obtained some

[87]Jour. Roy. Geol. Soc. Ireland, 2d ser., Vol. 4, Part 3, 1876, p. 140.
[88]Trans. St. Louis Acad. Sci., Vol. 3, No. 2, 1875, p. 246.
[89]Zeitschr. Deutsch. geol. Gesell. Prot., Vol. 56, 1904, p. 127.
[90]Mono. U. S. Geol. Survey, Vol. 31, 1898, p. 208 ff.

valuable data bearing on the problem. Thermal springs, attaining a temperature of 120° F., rise through fissures in the same limestone formation here that exhibits local dolomitization effects at Aspen, and the analysis of samples of the limestone taken at intervals from the conduits of the springs outward showed a progressive, though in some cases almost an inappreciable, decrease in the magnesia content. The conclusion was reached, therefore, that the local dolomitization at Aspen is probably due to the effects of hot springs which, rising along faults and fractures, altered the limestone to dolomite by means of the $MgCO_3$ and $MgCl_2$ they held in solution.

By Van Hise[91] the importance of dolomitization through the agency of ground water is strongly emphasized, and it would appear that he gives this method of dolomite formation precedence over dolomitization beneath the sea.

Local dolomitization phenomena along fissures in the Carboniferous limestone of South Wales is attributed to the action of ground water by Dixon[92], who states that water percolating downwards from the surface effected the change. Wichmann[93] likewise has described local dolomitization effects in the Korallenoolith (Jura) which he ascribes to the action of ground water bearing $MgCO_3$.

The latest word expressed upon the efficiency of ground water in producing dolomitization is that of Steidtmann[94], who regards this method of dolomite building as capable of operating only locally.

C. The Pneumatolytic Alteration Theory.—The pneumatolytic theory of the origin of dolomite was introduced in 1779, by Arduino,[95] to whom we are indebted for the first attempt to explain the formation of the rock. Dolomite had not been fully differentiated from limestone at that time, but Arduino mentions a magnesian limestone which from its association with rocks of volcanic origin he believed to have been formed by the alteration of ordinary limestone during volcanic activity.

[91]Mono. U. S. Geol. Survey, Vol. 47, 1904, p. 804 ff.
[92]Geology of the South Wales Coal Fields, Part 8: Mem. Geol. Survey, England and Wales, 1907, p. 13.
[93]Zeitschr. Deutsch. geol. Gesell., Vol. 61, 1909, p. 392.
[94]Jour. Geol., Vol. 19, 1911, p. 323.
[95]Cited by Morlot, Haidinger's Naturw. Abh., Vol. 1, 1847, p. 305.

Heim[96] also entertained similar views as to the origin of the rock, but it remained for Von Buch[97] to develop the theory and put it in definite form in the early twenties of the last century. In his studies in the Tyrol he observed that the dolomite was vesicular; that the bedding planes and the fossils were obliterated and that a brecciated, fissured and crystalline structure had been taken on. He, therefore, concluded that this could represent no original deposit from the sea, but that it must have been deposited at first as limestone and subsequently altered. This alteration, he believed, was accomplished by volcanic vapors bearing magnesia, which were given off by the intrusions of augite porphyry which there penetrate the rock. This view, however, was not shared by Wissmann[98] nor by Fournet,[99] who were unable to find any constant association of the dolomite with the intrusives.

In 1843, Klipstein[100] adopted the pneumatolytic theory to explain the veinlike deposits and irregular masses of dolomite in the transition limestone of the Lahn district, holding that ascending magnesian vapors had effected the transformation, although he was not able to find fissures extending downwards from the dolomite in all cases. Likewise Coquand[101] believed that dolomites associated with igneous intrusions were of pneumatolytic origin, and in support of his contention he furnishes quite convincing evidence. Thus, at Rougiers, in the province of Var, in France, samples of the limestone associated with basalt intrusions showed a progressive decrease in the magnesia content from limestone imbedded in the basalt, which contained 39.6 per cent of $MgCO_3$, to limestone two meters away which bore only 9.5 per cent. The unaltered limestone not associated with igneous rocks showed no trace of magnesia. The force of this argument, however, has been weakened by the observations of Bischof,[102] who held that this phenomenon might

[96]Cited by Zirkel, Lehrbuch der Petrographie, 2d ed., Vol. 3, 1894, p. 505.
[97]Cited by Morlot, Haidingers Naturw. Abh., Vol. 1, 1847, p. 305.
[98]Cited by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 200.
[99]Bull. Soc. géol. France, 2d ser., Vol. 6, 1849, p. 502.
[100]Cited by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 187.
[101]Bull. Soc. géol. France, Vol. 12, 1841, p. 314.
[102]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 179.

19

be due to the local alteration of the limestone by $MgCO_3$ liberated by the decomposition of the basalt.

Karsten[103] also favored the volcanic theory as elaborated by Von Buch, and Frapolli[104] similarly has gone on record in favor of this view, holding that the dolomites were formed through the agency of volcanic emanations either while deposition was going on beneath the sea or after the rock was deposited. Quite the same opinion was held by Durocher[105] who, basing his supposition upon the conditions of his experimental production of dolomite, believed that vaporous $MgCl_2$ emanating from the interior of the earth had metamorphosed limestone to dolomite.

The latest writer to express himself on this theory is Linck,[106] who states that dolomite might be formed under favorable conditions by pneumatolytic action.

III. Leaching Theories.

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

A. Surface Leaching Theory.—The view that dolomite might result from surface leaching seems to have been first suggested by Apjohn[107] in 1838, who stated that the $CaCO_3$ might be removed from limestones containing some magnesia by the solvent action of carbonated waters, and that some dolomites might have been produced in this manner. Grandjean[108] subsequently was led to adopt the same explanation, in 1844, to account for the dolomites of the lower Lahn district, and pointed out that the dolomite is developed to its greatest extent near fissures and cracks in the limestone where water has had easy access.

[103]Archiv. Min., Vol. 22, 1848, p. 545.
[104]Bull. Soc. géol. France, Vol. 4, 1847, p. 832.
[105]Compt. Rend., Vol. 33, 1851, p. 64.
[106]Doelter's Handbuch der Mineralchemie, Vol. I, 1912, p. 134.
[107]Jour. Geol. Soc. Dublin, Vol. 1, 1888, p. 368.
[108]Cited by Bischof, Elements of Chemical and Physical Geology. English translation, Vol. 3, 1859, p. 193.

The same view was accepted by Sandberger[109] the following year for the dolomites of the same district.

In support of this theory also are the observations of Bischof,[110] who showed by experiment that carbonated waters do not dissolve out of magnesian limestone more than a mere trace of magnesia and concluded that dolomite would ultimately be formed either by the action of surface water, or of sea water on limestone. He remarks that "it may be conjectured that the dolomite containing calc-spar druses is still in course of formation, while in that containing bitter-spar druses the conversion is complete" and sums up with the following statement:

Considering all the circumstances, it appears probable that limestone containing little or no silicates, but rich in magnesia, may be converted into dolomite on the spot, by extraction of the excess of calcium carbonate.

Hardman[111] also regarded this as the plausible theory of dolomite formation, and he sought by its employment to explain the method of origin of the Carboniferous dolomites of Ireland. He actually proved experimentally that the magnesia of these limestones became more concentrated when they were subjected to the action of carbonated waters and showed by analysis that the stalactite and stalagmite deposits of caves in the magnesian limestone were extremely low in magnesia. These features, together with the porous character of the dolomite, seemed to him to speak forcibly for the leaching hypothesis.

In still later times Hall and Sardeson[112] favored this theory in their discussion of the origin of "The Magnesian Series of the Northwestern States." Thus:

The flow of waters from the dolomitic beds, with their load of calcium carbonate, can in time produce but one result, and that is to bring into more equal proportions the quantity of calcium and magnesium carbonates. The disappearance of over 80 per cent more of the former than of the latter, which

[109]Neues Jahrb., 1845, p. 577.
[110]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 195.
[111]Proc. Roy. Irish Acad., 2d ser., Vol. 2, (Science), 1875-77, p. 705.
[112]Bull. Geol. Soc. America, Vol. 6, 1895, p. 167.

occurs if the original rock of these beds had the composition of average modern marine deposits, must result in the removal of at least eight times as much of that material as remains behind. Under such an assumption every 100 feet of the present thickness of the Oneota and Shakopee would represent an original thickness of 1,000 feet, more or less, an extent much nearer in accord with what seems necessary in sedimentary accumulations to conform to the profound faunal changes and crustal movements so conclusively proved by the paleontologic and structural conditions of the rocks.

Phillipi,[113] in like manner, brought the leaching theory to bear, in 1899, to account for the Conchodon dolomite of the southern Alps. He points out that in the heights where the rock is subjected only to the action of water poor in CO_2 it is but little if at all dolomitized, but in situations where the water can take up CO_2 and humus acids, leaching and recrystallization have taken place. By him humus acids are regarded as the most powerful agents in transforming a weakly dolomitic limestone to dolomite.

B. *The Marine Leaching Theory.*—That marine leaching of calcareous deposits low in magnesia might give rise to dolomite was suggested by Bischof in 1859,[114] but he made no attempt to elaborate the idea. Eleven years later Gümbel,[115] in making a study of certain deep sea oozes, found one taken from a depth of 2,350 fathoms in the Atlantic which yielded upon analysis 1.44 per cent of magnesia. This magnesia content is accounted for upon the basis of the solution of a portion of the original calcareous material, and it is suggested that by the same method dolomitic rocks and marly intercalations might be formed.

The marine leaching theory, however, has been most fully developed by Högbom.[116] This writer regards marine leaching as far more important than surface leaching, since the latter can operate only on that portion of the limestone exposed. The results of a leaching experiment on a marl demonstrated the plausibility of this process, and the following table of analyses of deep sea deposits taken from the Challenger report also seemed to lend support to this view.

[113]Neues Jahrb., 1899, Vol. 1, p. 32.
[114]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, [115]Neues Jahrb., 1870, p. 753.
p. 195.
[116]Neues. Jahrb., Vol. I, 1894, p. 262.

TABLE V.

CaCO₃ Range	CaCO₃ Average	MgCO₃	Parts of MgCO₃ to 100 Parts of CaCO₃	Number of Analyses
80-100	86.7	0.7	0.8	8
60-80	68.3	1.4	2.0	8
40-60	52.0	1.2	2.4	8
20-40	32.0	0.9	3.0	3
10-20	16.2	1.6	10.0	4
5-10	6.1	0.7	11.5	1
3-5	3.7	1.6	43.0	7
1-3	2.0	2.1	105.0	9

The most convincing argument of all, however, was found by Högbom in the marine Quaternary marls of Sweden. These marls, which are believed to have been transported from a Silurian argillaceous rock by glacial waters, become progressively weaker in CaCO₃ and richer in MgCO₃ the farther southward one goes from the parent rock, as shown by analyses made by the Geological Survey. (See Table VI.)

TABLE VI.

Section	CaCO₃	MgCO₃	Parts of MgCO₃ to 100 Parts of CaCO₃	Number of Analeses
Leufsta	32.0	1.2	3.7	14
Örbyhus	23.0	1.4	6.1	6
Salsta	21.7	1.5	6.9	10
Upsala	17.8	1.3	7.2	8
Sigtuna	11.4	0.8	7.0	29
Fånö......................	11.9	1.9	16.0	9
Södertelje	7.6	2.8	37.0	9
Hörningsholm	3.3	1.2	36.0	17

This relationship is explained by the fact that the longer the glacial mud was in suspension and the farther it was carried from the source, the more the CaCO₃ was leached out and the MgCO₃ enriched because of its greater insolubility.

Högbom also furnishes evidence of enrichment of magnesia by marine leaching in the coral reefs of Bermuda. Analyses of the reef-building corals and other organisms showed a uniformly low magnesia content, but the lagoon muds which must

have been derived from the organisms of the reef were found to be much richer in this constituent, one sample yielding 4.04 per cent of $MgCO_3$. Likewise the magnesia content was found to increase with the degree of fineness and duration of suspension. Thereupon it is suggested that if the detritus should remain in suspension long enough it would undergo thorough leaching and a true dolomitic sediment might result. The opinion is then ventured that many dolomites of older formations played an important part in the building of the Alpine dolomites.

Judd[117] is of the opinion that the dolomitic rock disclosed by the boring at Funafuti was formed, in part at least, by marine leaching. The conditions represented there are summarized briefly as follows:

As has been already pointed out, the proportion of $MgCO_3$ rises in the first 50 feet of descent in all the borings, from the normal 1 to 5 per cent, up to a maximum of nearly 16 per cent which is attained at a depth of about 25 feet, and then declines again to what may be considered the normal amount, 1 to 5 per cent. At 637 feet the percentage of $MgCO_3$ again rises from the normal and by 660 feet has reached nearly 40 per cent. This proportion, with some small exceptions, is maintained to the bottom of the bore hole at 1,114 feet.

Cullis,[118] who made a mineralogical study of the core, states that above the 637 foot level the rock consists of aragonite and calcite without individualized dolomite. But from this depth to the bottom of the hole the rock is made up of calcite and individualized dolomite.

In reviewing the evidence in favor of marine leaching, Judd refers to the analyses of Lithothamnium by Högbom, which showed a maximum of 14 per cent of $MgCO_3$ and regards it as probable that this abnormal magnesia content is due to leaching, since the material originally secreted by these organisms probably did not contain more than one per cent of $MgCO_3$. He concludes that "it seems not improbable that the enrichment of the rock in $MgCO_3$ up to 16 per cent in the upper part of the cores may be entirely due to the leaching out of

[117]The Atoll of Funafuti, 1904, p. 362.
[118]Idem., p. 393, ff.

the CaCO$_3$.'' All of the MgCO$_3$ of the rock to a depth of 637 feet, then, according to him, probably is to be ascribed to leaching, and the variation in the magnesia content at different levels is due to the varying proportions of organisms which differ in their susceptibility to the leaching out process. Judd then suggests that a rock so enriched in magnesia by leaching might exercise an attractive action on the magnesium salts of the sea water. He evidently would imply that this might account for the more highly dolomitic rock in the lower part of the boring, but he does not express himself clearly on this point.

This view, however, is not esteemed highly by Skeats,[119] who, in reference to Judd's conclusions, remarks as follows:

The process of differential solution is one which no doubt coral-limestones undergo to a greater or smaller extent, and it is probably the correct explanation of the origin of the all but structureless limestones containing magnesium-carbonate in sufficient amount for the production of dolomite-crystals. Very extensive solution and removal of calcium-carbonate is needed, however, before the percentage of magnesium-carbonate in the residual rock is appreciably raised. Assuming the original limestone to contain 1 per cent of magnesium-carbonate, an amount which is probably near the superior limit for the fresh organisms composing the rock, and further, assuming that only the calcium-carbonate is dissolved by carbonated water 80 per cent of the original rock must be removed by solution before the magnesium-carbonate in the remainder reaches 5 per cent, 90 per cent must be dissolved before the magnesium-carbonate reaches 10 per cent, and over 93 per cent before the magnesium-carbonate reaches 16 per cent. So extensive a removal of the original substance of the rock would largely destroy the structure of the organisms that it contained. In the case of the limestones from Christmas Island, Niue, and elsewhere, examined by me, in which magnesium-carbonate was present in the rock in amounts up to 11 per cent, the structure of the contained organisms was in general wonderfully preserved; and not only was there no evidence of solution in the rock, but on the contrary secondary calcite and secondary aragonite were deposited upon the organisms to a considerable extent. I was in consequence, forced to the conclusion that in these limestones

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[119]Neues Jahrb., Vol. 1, 1894, p. 262.

the magnesium-carbonate was introduced into the rock from the sea-water, resulting in the partial replacement of calcium- by magnesium-carbonate.

Peach and Horne[120] are favorable to the idea that marine leaching may account in part for the Cambrian dolomites of the Northwest Highlands of Scotland, suggesting that unicellular plants which secreted lime may have existed in the plankton as in the sea today and that the small magnesia content of these may have been concentrated by the abstraction of the more soluble $CaCO_3$. They believe, however, that some replacement has taken place also.

Murray and Hjort[121] also concur that the explanation of en- richments of magnesia in deep sea deposits is to be sought in preferential dissolution of the lime. To them enrichment of the magnesia by reaction with sea water does not seem plausi- ble, since this would require that the waters be concentrated with $MgCO_3$.

EXPERIMENTAL EVIDENCE.

As regards the experimental evidence of the origin of dolo- mite, it may be safely said that the present data are very un- satisfactory and of little value in interpreting the conditions under which this rock is formed in nature. Dolomite has been prepared repeatedly at high temperature and at high pressure, and at both high temperature and high pressure, but in only rare instances has it been prepared artificially at ordinary tem- perature and pressure, and then only in minute amounts and for the most part under conditions which doubtfully obtain in nature, at least on a large scale.

I. Evidence Bearing on the Primary Deposition Theories.

The experimental evidence bearing on the primary deposi- tion of dolomite is, from the nature of the case, applicable only to the theory of chemical precipitation. The experiments bear- ing on this theory are for convenience classified as follows: (1) those performed at ordinary temperature and ordinary pres- sure; (2) those performed at elevated temperature but at ordi-

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[120]The Geological Structure of the Northwest Highlands of Scotland; Mem. Geol. Survey, Great Britain, 1907, p. 370.
[121]The Depths of the Ocean, 1912, p. 180, ff.

nary pressure; and (3) those performed at ordinary temperature but at elevated pressure. These will be discussed in their regular order.

Experiments at Ordinary Temperatures and Pressures.— All attempts to produce dolomite directly under ordinary conditions have failed, but evidence of the possible production of dolomite under these conditions in nature has been observed in several instances. Thus, Moitesser[122] found small rhombohedral crystals which had the composition of dolomite, in a badly closed flask of mineral water from a French spring. Similarly, Terreil[123] reported that rhombohedral crystals of carbonate of calcium and carbonate of magnesium were deposited upon the walls of sealed tubes which contained samples of mineral water from the region of the Dead Sea. He does not distinctly state that the double carbonate was present, but remarks that this discovery may have an important bearing on the origin of the dolomites of that region.

Certain travertine deposits also are said to be rich in $MgCO_3$. F. W. Clarke[124] states that "according to J. Giradin, the travertine formed by the mineral spring of Allyne, near Clermont, in France, is rich in magnesium carbonate. In recent travertine he found 28.80 per cent of $MgCO_3$ with 24.40 of $CaCO_3$, and in old travertine the proportions were 26.86 and 40.22 respectively. Whether this represents a dolomite or a mixture of the carbonates was not determined."

J. F. Johnson[125] has likewise described a dolomitic spring deposit on the north bank of the river Tees in England, and believes this occurrence has a direct bearing on the origin of dolomites in general. Gorup-Besanez, however,[126] states that the springs which issue from the dolomites of the Jura deposit upon evaporation the mixed carbonates of calcium and magnesium although they are present in essentially the same proportions as in normal dolomite. Bischof[127] has this to say regarding the magnesia content of spring deposits:

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[122]Jahresber. Chemie, 1866, p. 178.
[123]Cited by Lartet, Bull. Soc. géol. France, 2d ser., Vol. 23, 1866, p. 750.
[124]Bull. U. S. Geol. Survey, No. 491, p. 536.
[125]Liebig and Kopp, Jahresber., 1853, p. 927.
[126]Quoted by F. W. Clarke, Bull. U. S. Geol. Survey No. 491, p. 536.
[127]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 167.

Water extracts from a mixture of carbonates of lime and magnesia twenty-eight times as much carbonate of magnesia as carbonate of lime; consequently, when water containing about equal quantities of these carbonates, evaporates so far that the separation of carbonate of lime commences, the deposition of carbonate of magnesia cannot take place until the water has evaporated to such an extent that there remains only 1-28 of the water present when the deposition of lime commenced. When the amount of carbonate of magnesia is less than that of the carbonate of lime, it is evident that the evaporation must extend still further before the deposition of carbonate of magnesia can commence. Then since it generally happens that spring water contains less carbonate of magnesia than carbonate of lime, it is clear that by the evaporation of this water the greater part of the carbonate of lime will be deposited without any trace of carbonate of magnesia being mixed with it. When the water of a spring does not evaporate completely, but if somewhat less than 27-28 is evaporated, carbonate of lime alone will be deposited, and the whole of the carbonate of magnesia may be retained in solution. If at the same time the deposits from such spring water contain traces of magnesia, its deposition must be attributed to the tendency towards the production of a double salt with carbonate of lime. This may, perhaps, be the case with the dolomite marl, shelly limestone, and mixtures of limestone and dolomite examined by Karsten. The composition of the deposits from the water of springs shows, moreover, that true dolomite, or the compound of carbonates of lime and magnesia in equal equivalents, is never deposited from water.

As above stated, all attempts to produce dolomite artificially as a direct precipitate under ordinary conditions have been unsuccessful. Scheerer[128] failed to obtain it by mixing solutions of $CaCO_3$ and $MgCO_3$ together in different proportions and evaporating at ordinary temperatures. The two carbonates were thrown down separately as characteristic rhombohedrons of calcite and prisms of hydrous magnesium carbonate. Similar results were obtained by Gorup-Besanez and later by Hoppe-Seyler[129] when they allowed a carbonic acid solution of the two carbonates to evaporate slowly. Leitmeier[130] has repeated this experiment recently, evaporating the solutions at temperatures of from 10° to 100°, but his results also were negative.

[128]Neues Jahrb., 1866, p. 1.
[129]Quoted by F. W. Pfaff, Neues Jahrb, Beil. Bd. 23, 1907. p. 555.
[130]Doelter's Handbuch der Mineralchemie, Vol. I, 1912, p. 395.

The experiments of the writer along this line likewise have been unsuccessful. Separate solutions of the bicarbonates of calcium and magnesium after being standardized were mixed in molecular equivalent proportions so as to give the same ratio of $CaCO_3$ to $MgCO_3$ as exists in normal dolomite. The solution was then allowed to evaporate spontaneously during a period of one month. It was noted that the carbonates came down separately with the $CaCO_3$ much in advance of the $MgCO_3$ which was deposited in the hydrous form ($MgCO_3.3H_2O$). Negative results still were obtained when a solution prepared as above was inoculated with a crystal of dolomite and allowed to evaporate. The crystal did not grow and no dolomite could be found in the residue. Nor could the double carbonate be prepared by evaporating spontaneously a solution of the two carbonates obtained by the action of carbonated waters on normal dolomite, even when a dolomite crystal was introduced and a concentrated solution of NaCl and magnesium salts was introduced.

The experiments of Murray and Irvine[131] on the power of $(NH_4)_2CO_3$ furnished by decomposing organic matter to precipitate $CaCO_3$ and $MgCO_3$ from sea water are interesting in this connection. In general these show that $CaCO_3$ may be deposited in large amount through this agency, but that little $MgCO_3$ is precipitated, thus:

Nine small crabs weighing in all 11 ounces were placed in a shallow glass vessel containing 2 litres of ordinary sea water and were fed on mussel flesh. The water was never removed nor aerated, the effete matters passing into it. At the end of fourteen days all the crabs had died and were removed. The water being then in a putrid condition, it was set aside for about three weeks at a temperature ranging from 70° to 80° Fahr. All the conditions of the last two experiments were observed and it was found that crystals of carbonate of lime had been thrown down in amount practically equivalent to all the calcium present in the sea water employed.

Similar results were obtained when the effect of urine on sea water was tried. After the mixture had stood for seven days at temperatures ranging from 60° to 80° F. the precipitate thrown out had the following composition:

[131]Proc. Roy. Soc. Edinburgh, Vol. 17, 1889, p. 79.

	Per cent
Water and organic matter containing ammonia, 7.38 grains	31.81
Carbonate of lime	4.85
Phosphate of magnesia and ammonia	51.10
Phosphate of lime	12.24
	100.00

Upon allowing the filtrate from the above experiment to stand ten days more under the same conditions, practically all the soluble calcium salts in the sea water were precipitated. The composition of the precipitate was:

	Per cent
Water and organic matter	20.25
Carbonate of lime	75.35
Carbonate of magnesia	1.02
Phosphate of magnesia	3.38
	100.00

The results of these experiments are wholly in accord with the following statement of these investigators:

In the laboratory, when carbonate of ammonia is added to sea water, nine tenths of the calcium in solution is thrown out as carbonate of lime, while the magnesia salts remain in solution; so that if the reaction above indicated be that which takes place in the ocean, then to this circumstance may be due the fact that carbonate of magnesia is almost wholly absent from recent coral reefs and deep-sea calcareous formations.

The efficiency of decaying organic matter as a precipitant of calcium and magnesium has also been studied by Fischer,[132] who arrived at similar conclusions. Upon placing decaying organisms in ordinary sea water he obtained a precipitate overnight consisting of 94.45 per cent of $CaCO_3$ and 5.55 of $MgCO_3$. Neither concentration of the sea water and of the decaying organic matter, nor increase in temperature served to appreciably increase the magnesia content of the precipitate.

Experiments at Elevated Temperatures and Ordinary Pressures.—Dolomite has been prepared artificially at elevated temperatures by several investigators. Forchhammer,[133] upon adding water containing $CaCO_3$ to boiling sea water, obtained a pre-

[132]Monatsh. Deutsch. geol. Gesell., 1910, p. 255.
[133]Quoted by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 161.

cipitate containing 12.23 per cent of $MgCO_3$ and 87.77 of $CaCO_3$, and when Na_2CO_3 was added as well as $CaCO_3$, the $MgCO_3$ content of the precipitate was increased to 27.93 per cent. It is not made clear, however, whether the double carbonate was formed or not in these experiments.

An analogous experiment was performed by Hunt.[134] A solution of the chlorides of calcium and magnesium, which had been accidentally mixed with a quantity of Na_2CO_3 insufficient for its complete decomposition, was set aside for a period of five weeks. At the end of this time the solution still retained a portion of the $MgCl_2$, but possessed only a trace of $MgCO_3$. The precipitate, after heating, analyzed $CaCO_3$ 50.52, $MgCO_3$ 30.09 and water 19.39 per cent.

The experiments of Linck[135] are interesting in this connection. When one molecular weight of $MgCl_2$ and one molecular weight of $MgSO_4$ were dissolved in 500 cc. of water and mixed with a solution of one and one-half molecular weights of ammonium sesquicarbonate in 150 cc. of water, the resulting solution remained clear, but when one molecular weight of $CaCl_2$ in 100 cc. of water was added a voluminous precipitate came down. This became crystalline when warmed to about 30° C. and examination of the material showed it to consist of minute round or oval spherulitic grains which had essentially the same composition as normal dolomite, but their double refraction was weakly positive, showing that they could not be this mineral. The same reaction took place when the magnesium salts were used separately but in double the amount of the above experiment. But the effect of NaCl when added in about the same proportion as it exists in sea water was to reduce the $MgCO_3$ content of the precipitate to 12 per cent. The same effect, however, did not result when one molecular weight of Na_2CO_3 was added to the NaCl solution beforehand, for then the residue yielded 49 per cent. Briefly these results may be explained as follows: The effect of adding NaCl to the solution was to repress the ionization of the $MgCl_2$, since these two compounds have one ion in common. For the same reason the addition of

[134]Am. Jour. Sci., 2d ser., Vol. 42, 1866, p. 56.
[135]Montash. Deutsch. geol. Gesell., 1909, p. 230.

Na_2CO_3 tends to increase the yield of $MgCO_3$. The concentration of the carbonate ions in solution is increased with the result that the $MgCO_3$ of the solution becomes less dissociated and as a consequence must be deposited, since the solution is already saturated with the undissociated salt. As above stated, the precipitate obtained in these experiments did not behave as dolomite. Nor was it transformed to this mineral even when heated to 110°. But when solutions prepared as above were warmed several hours in sealed tubes at 40 to 50° C., spherulites possessing negative double refraction and all other properties of dolomite were obtained. Analysis of these gave 44.8 per cent of $MgCO_3$ and 49.5 of $CaCO_3$. Linck, therefore, was led to suggest that dolomite might be formed in the sea in this manner, since decaying organisms give off ammonium carbonate. Meigen,[136] however, who has repeated Linck's experiment, calls this in question, since he failed to procure dolomite under these conditions, but obtained only a product easily soluble in dilute acetic acid.

Bourgeois and Traube[137] also report the production of dolomite as a direct precipitate at elevated temperature. Thus, by heating a solution of $MgCl_2$, $CaCl_2$ and KCNO (potassium cyanate) to 130° in a sealed tube dolomite was produced. But as F. W. Clarke has pointed out, this experiment has no geological significance.

The experiments of Bischof[138] have a much more important bearing on the problem, although only the mixed carbonates were produced in these. First, solutions of carbonate of calcium and of carbonate of magnesium in carbonic acid water, were mixed in the proportion of two parts of magnesium to one of calcium and evaporated at a temperature of 122° F. After one-third of the solution had evaporated the precipitate contained 1.64 grs. of $CaCO_3$ and 1.99 grs. of $MgCO_3$. When the filtrate from the above was next evaporated to one-fifth the original volume it was found to consist of only a trace of $CaCO_3$ and of .43 grs. of $MgCO_3$. It will be noted that in this experiment the

[136]Quoted by Leitmeier, Doelter's Handbuch der Mineralchemie, Vol. I, 1912, p. 395.
[137]Quoted by F. W. Clarke, Bull. U. S. Geol. Survey No. 491, p. 537.
[138]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 168.

$MgCO_3$ was considerably in excess of the $CaCO_3$ in the solution. In the next experiment this factor was eliminated by using well water which contained only about half as much $MgCO_3$ as $CaCO_3$. Eighty ounces of this water was evaporated at 122° F. After 45 ounces was evaporated, 8.36 grs. of $CaCO_3$ had been deposited, but only a trace of $MgCO_3$. When the remaining 35 ounces was evaporated, however, the residue was found to contain 1.95 grs. of $MgCO_3$ and only .22 grs. of $CaCO_3$. When this experiment was repeated more carefully it was found that the $MgCO_3$ did not begin to deposit until seven-eighths of the water had evaporated, and almost all the $CaCO_3$ had been thrown out. Bischof then draws the following conclusions:

It follows also from these experiments that the production of a double carbonate of lime and magnesia cannot take place to any considerable extent, if at all, by the evaporation of water similar to the above, and under analogous conditions. In evaporation at the ordinary temperature, also, the quantity of water evaporated before deposition takes place must be very considerably greater than when the evaporation takes place at a higher temperature.

The elaborate series of experiments of F. W. Pfaff[139] bearing on the direct deposition of dolomite should also be mentioned here. First Na_2CO_3 was added to solutions of $CaCl_2$ and $MgCl_2$, and of $CaCl_2$ and $MgSO_4$, and evaporation allowed to take place on the water bath. But no dolomite was obtained. Similarly the addition of ammonium carbonate to a solution corresponding to sea water in composition failed to yield the double carbonate upon addition of ammonia and evaporation. Next a saturated solution of NaCl with $CaCO_3$ and $MgCl_2$ through which CO_2 was passed was evaporated to dryness without results. The substitution of $MgSO_4$ for $MgCl_2$ was still without effect. Then carbonated solutions of $CaCO_3$ were treated separately with $MgCl_2$ and $MgSO_4$ and to each was added $(NH_4)_2CO_3$. Evaporation again yielded no dolomite. The addition of $(NH_4)_2CO_3$ to a carbonated solution of $CaCO_3$ and $MgCO_3$ was likewise without results. Negative data were still obtained when a strong solution of $CaCO_3$ and magnesia alba was treated with CO_2 and evaporated. When, however, the

[139]Neues Jahrb., Beil. Bd. 9, 1894, p. 485.

preceding experiment was repeated using $(NH_4)_2CO_3$ instead of CO_2 and the solution evaporated on the sand bath, at a temperature which attained 140° C., towards the last, a crystalline residue difficultly soluble in dilute acid was obtained. But evaporation to dryness of a solution prepared in the same manner on the water bath yielded a readily soluble precipitate.

Another series of experiments next undertaken to determine the influence of $(NH_4)_2S$ and H_2S in the formation of dolomite met with much more success. First a saturated solution prepared by the action of $(NH_4)_2S$ on the carbonates of calcium and magnesium was evaporated to dryness with the addition of $(NH_4)_2CO_3$. The process took several days, but in the end the residue contained double refracting crystals which dissolved in strong acid only when it was heated. Since it was not certain that the temperature did not rise above 100° in this operation the experiment was repeated, and the evaporation was conducted this time on the water bath. A residue with similar properties was obtained, analysis of which showed considerable magnesia and some lime. Similar results were obtained when an H_2S solution was substituted for the $(NH_4)_2S$ solution and NaCl was added. This time the $(NH_4)_2CO_3$ was omitted, but CO_2 was passed through while evaporation proceeded at 50° to 60° C. The precipitate behaved as in the preceding experiment, and analysis showed only a small amount of lime. Pfaff suggests that this product may have consisted of magnesite with some lime. When $(NH_4)_2S$ was used in place of H_2S under somewhat similar conditions, rhombohedrons which showed diagonal extinction were obtained. These effervesced at first in strong acid, but a residue remained which dissolved only when heat was applied. An analysis of this product by Professor Hoppe-Seyler gave:

	Per cent
$CaCO_3$	12.77
$MgCO_3$	79.84
Fe_2O_3	1.74
Insoluble	4.64
H_2O	1.00

Since the magnesia was much in excess of the lime in the above experiment the operation was repeated using these con-

stituents in the proportion of one to one, but this was no more successful, for only 6.93 per cent of $CaCO_3$ was obtained. The precipitate evidently represented magnesite with $CaCO_3$ mechanically mixed. Further trials under slightly different conditions still failed to increase the yield of the $CaCO_3$ to the normal dolomite ratio. When, however, the solutions prepared by the action of the sulphides of H_2S and $(NH_4)_2S$ on the carbonates of calcium and magnesium were mixed in the proportion of two of calcium to one of magnesium, the results were much more satisfactory. After NaCl was added to the mixture prepared in this manner and CO_2 passed through for slightly more than two months the precipitate was washed and dried at 120° C. Analysis showed it to have the following composition:

	Per cent
$MgCO_3$	43.7
$CaCO_3$	52.0
Insoluble	3.8

Recalculation to eliminate the insoluble matter gave 45 per cent of $MgCO_3$ and 54 of $CaCO_3$, almost exactly the same proportions as in normal dolomite. When the experiment was repeated without NaCl no trace of dolomite was obtained after a period of fourteen days.

Experiments at Ordinary Temperatures and Elevated Pressures.—For experiments bearing on the production of dolomite at ordinary temperatures but at elevated pressures we are indebted entirely to F. W. Pfaff.[140] His attempts to produce dolomite as a direct precipitate were unsuccessful, but he obtained it as an alteration product under a variety of conditions. It was sought to prepare the double carbonate as a direct precipitate in the following manner: $CaCO_3$ and magnesium alba were added to a saturated solution of NaCl. CO_2 was then passed through under a pressure of 2 to 2½ atmospheres. When the solution became saturated with calcium and magnesium the pressure was decreased, but seldom was a precipitate formed, and evaporation gave rise only to the deposition of $CaCO_3$ and hydrous $MgCO_3$, separately.

[140]Neues Jahrb., Beil. Bd. 9, 1894, p. 485.

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Since the basic-carbonate of magnesium obtained in such experiments is in no condition to unite with $CaCO_3$ to produce dolomite, it was attempted by Pfaff in a later series of experiments[141] to produce anhydrous $MgCO_3$. The effect of solutions of potassium and sodium carbonate on $MgCl_2$ at high pressures was tried without avail. The addition of a concentrated solution of $CaCl_2$ or of $NaCl$ also failed to produce the anhydrous salt. The results were equally unsatisfactory when a solution of magnesium salts was subjected to the action of $(NH_4)_2CO_3$ for 48 hours at 500 atmospheres. Pfaff, therefore, concludes that dolomite and anhydrous $MgCO_3$ are not precipitated directly under high pressure.

Discussion.—To recapitulate, experiments have failed to indicate the conditions under which dolomite can be precipitated directly at ordinary temperatures and pressures. But there is convincing evidence that dolomites have been so formed, on a small scale at least, in nature. The fact that the two carbonates are found by experiment to come down separately with the $CaCO_3$ much in advance of the hydrous $MgCO_3$ cannot, therefore, be regarded as wholly opposed to the theory of chemical deposition of large masses of dolomite, for under favorable conditions the double carbonate may be precipitated directly, the dolomite molecule being continuously formed in solution while deposition proceeds. The chief objection to the chemical theory thus falls down. But the fact that experiments have failed to give rise to a magnesia-rich precipitate from sea water at ordinary temperature, even when the pressure was elevated, must be regarded as important.

The experiments carried on at elevated temperature and ordinary pressure show that the double carbonate is readily formed under these conditions, but while these may have a direct bearing on the origin of some local dolomites they cannot be considered as having an important bearing on the origin of stratified dolomites of great thickness.

II. Evidence Bearing on the Alteration Theories.

Experiments at Ordinary Temperatures and Pressures.— As regards the evidence bearing on the production of dolo-

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[141] Neues Jahrb., Beil. Bd. 23, 1907, p. 529.

mite as an alteration product under ordinary conditions, a number of experiments may be mentioned. Thus, Bischof,[142] trying the effect of a solution of $MgCO_3$ upon carbonate of lime, found that "after twelve hours there was neither any lime in solution, nor any magnesia retained by the carbonate of lime." A similar experiment was tried using small fragments of chalk instead of powdered carbonate of lime. "The closed vessel stood for several years unopened, but examination from time to time failed to reveal any action upon the edges of the chalk fragments." Scheerer,[143] however, later recorded somewhat different results from a similar experiment. When powdered chalk was treated with a carbonated solution of $MgCO_3$ for forty-eight hours with the passage of CO_2 it was found that nearly all of the $MgCO_3$ had gone into the sediment and that only a slight amount of the same remained in the solution, which was now rich in $CaCO_3$. But it is not stated that dolomite was formed.

Hoppe-Seyler[144] was unable to produce dolomite by the action of solutions of $MgCl_2$ on $CaCO_3$ for several months. The same negative result was obtained when a dilute $MgSO_4$ solution was saturated with $CaCO_3$ and a current of dry air drawn through for a long time. Even when NaCl was added to the saturated solution of $MgSO_4$ the residue yielded no dolomite and the freezing of an $MgSO_4$ solution saturated with $CaCO_3$ was equally unsuccessful. The effect of sea water on $CaCO_3$ was also tried but with no more success. Likewise when Liebe[145] immersed chalk a year and a half in $MgCl_2$ solutions of various concentrations no trace of decomposition could be detected.

More successful results, however, are reported by Leit-meier,[146] who in his experiments on the formation of aragonite claims to have prepared dolomite also. In these experiments .1 gram of powdered $CaCO_3$ in 100 grams of water was subjected to the action of .001, .005, .01 and .05 gram of $MgSO_4.7H_2O$ and $MgCl_2.6H_2O$ respectively. At low temperatures dolomite was obtained at none of these concentrations;

[142]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 167.
[143]Neues Jahrb., 1866, p. 1.
[144]Quoted by F. W. Pfaff, Neues Jahrb., Beil. Bd. 23, 1907, p. 555.
[145]Zeitschr. Deutsch. geol. Gesell., Vol. 7, 1855, p. 431.
[146]Neues Jahrb., Vol. 1, 1910, p. 49.

but at medium temperature (10° C.) a few fine grains which reacted as dolomite microchemically were obtained at the concentration of .01 gram. At a concentration of .05 gram, however, copious crystals which did not react with iron chloride were found in the residue. These showed partly developed crystallographic boundaries and appeared to possess the distorted structure characteristic of dolomite rhombohedrons. In the .1 gram solutions a much richer mixture of "dolomite" was obtained. The effect of higher temperatures was to produce essentially the same results, for "dolomite" was obtained at the same concentrations.

The experiments performed by F. W. Pfaff[147] at ordinary conditions are also interesting in this connection. By the action of a solution of $MgSO_4$, $MgCl_2$ and $NaCl$ on anhydrite with the passage of CO_2 a reaction product coating the anhydrite was obtained. This was soluble only in strong hydrochloric acid and had at one time the composition: $CaCO_3$ 61.7 per cent; $MgCO_3$ 38.7.

The experiments of the writer bearing on the artificial production of dolomite as an alteration product at ordinary temperatures and pressures have yielded no successful results. In these powdered aragonite was treated with solutions of known concentration of $MgCl_2$ and $MgSO_4$ and of definite mixtures of these salts. The influence of $NaCl$ and CO_2 on the reaction was also studied and the effect of inoculating the solutions with crystals of dolomite was tried. The concentration of the magnesium solutions used ranged from two to ten times the concentration of magnesium in ordinary sea water. After a period of six months and again after nearly three years the residues of the experiments were thoroughly tested microchemically for dolomite, but without successful results. Analyses of portions of the solutions, however, showed the presence of calcium in greater quantity than the solubility of $CaCO_3$ alone would account for, and there can be no doubt that a reaction had taken place, although no $MgCO_3$ had been deposited. Evidently the easily soluble trihydrate of magnesium carbonate had been formed.

[147]Neues Jahrb., Beil. Bd. 23, 1907, p. 529.

Experiments at Elevated Temperatures and Ordinary Pressures.—Dolomite has been prepared frequently as an alteration product at elevated temperatures and ordinary pressures. Morlot,[148] for instance, upon heating a mixture of one equivalent of sulphate of magnesium and two equivalents of powdered $CaCO_3$ to 392° F. in a sealed glass tube, obtained a mixture of dolomite and gypsum, and found that the $MgSO_4$ had been completely decomposed. Hunt,[149] however, found by repeating this experiment that the two carbonates did not crystallize out as dolomite.

The experiment of Sainte-Claire Deville[150] also should be mentioned here. A fragment of chalk after having been impregnated with a solution of $MgCl_2$ was placed in a platinum crucible and subjected to prolonged heating on the sand bath. At a temperature a little above 100° a reaction took place whereby $CaCl_2$ and dolomite were produced. By a single operation of this kind it was possible to replace only six to seven parts of lime by an equivalent amount of magnesia, but when the fragment was washed and subjected to the same procedure repeatedly the replacement went much further. Fragments of madrepores when subjected to the same treatment were replaced in a similar manner.

A somewhat similar experiment was performed by Sorby,[151] who attempted to produce a dolomite pseudomorph by the action of a solution of $MgCl_2$ on Iceland Spar at an elevated temperature. He found that only an external crust of $MgCO_3$ was formed by replacement.

The elaborate series of experiments by Klement[152] also has an important bearing on the problem of the origin of dolomite, although only the mixed carbonates were obtained.

The effect of $MgSO_4$ on aragonite was first observed. One-half gram of aragonite and 1.25 grams of crystalline $MgSO_4$ were placed in tubes, after which 10 cc. of a saturated solution

[148]Quoted by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 158.
[149]Am. Jour. Sci., 2d ser., Vol. 28, 1859, p. 170.
[150]Compt. Rend., Vol. 47, 1858, p. 91.
[151]Quart. Jour. Geol. Soc. London, Vol. 35, 1879, p. 56.
[152]Bull. Soc. Belge géol., Vol. 9, 1895, p. 12.

of NaCl was added and the tubes were sealed. A preliminary experiment having shown that at elevated temperature a re-action took place whereby $MgCO_3$ was deposited, the influence of time and temperature was studied. At a temperature of 50° to 55° C. only a trace of $MgCO_3$ was produced after an in-terval of ten days. The same was true when the temperature was held at 62° for four days, but after the same experiment ran for six days 1.3 per cent of $MgCO_3$ was formed. Above this temperature $MgCO_3$ was always obtained, and the amount increased directly with the time. Thus, at 72° for twenty-four hours he obtained 1.7 per cent, for sixty-seven hours 9.8 per cent, and for ninety-five hours 12.4 per cent. The maximum amount of $MgCO_3$, 38 per cent, was obtained at 90° for sixty-eight hours. When the heating was prolonged to one hundred and forty hours no increase was noted. By using another sample of aragonite, however, Klement was able to obtain 41.1 per cent of $MgCO_3$ after heating to 91° for one hundred and forty-four hours.

The influence of the changing of the concentration of the NaCl was then tried, the same amount of aragonite and $MgSO_4$ being used as in the preceding experiments. In general it was found that increase in the concentration of this constituent had the same effect as increase in time. For instance, it was found in a previous experiment in which a 10 cc. saturated solution of NaCl was used, that 24.5 per cent of $MgCO_3$ was formed at a certain temperature after a given time, but when now the 10 cc. saturated solution was diluted with 1 cc. of water the yield of $MgCO_3$ was reduced to 8 per cent under essentially the same conditions of temperature and time, and when the NaCl solu-tion used consisted of a 5 cc. saturated solution of NaCl plus 5 cc. of water only .6 per cent of $MgCO_3$ was obtained. When the NaCl was completely removed from the solution there was a still further reduction of the $MgCO_3$ content even when the $MgSO_4$ solution was very concentrated.

As regards the influence of the quantity of the reacting sub-stances it was found that when each was doubled there was a marked decrease in the amount of $MgCO_3$ produced. Klement

attempts to explain this on the assumption that equilibrium is soon reached under these conditions, since the volume of the solution is greater and the $CaSO_4$ produced by the reaction would not be so readily deposited. But this is difficult to understand.

The action of $MgSO_4$ on recent corals also was studied under the same conditions as in the first series of experiments. It was found that the powdered material gave even a greater yield of $MgCO_3$ than aragonite under similar conditions. The action of $MgSO_4$ on powdered calcite, however, was much less energetic. Thus, at 100° for ten hours in the presence of an excess of NaCl only a trace of $MgCO_3$ was formed, while at 90° for forty-eight hours 1.6 per cent of this compound was obtained.

The comparative efficiency of $MgCl_2$ in altering aragonite was likewise determined. When the $MgSO_4$ was replaced by an equivalent amount of this compound and 10 cc. of a saturated solution of NaCl was added the reaction proceeded very feebly, only .4 per cent of $MgCO_3$ being formed at 72° for 95 hours. When, however, only 3 cc. of a saturated NaCl solution was used instead of 10 cc. the yield was slightly increased, but it was still very low. These singular results are accounted for by Klement on the assumption that an easily soluble reaction product is formed here and that equilibrium is soon reached. This no doubt is important, but the effect of the NaCl in repressing the ionization of the $MgCl_2$ should also be taken into consideration.

Experiments at Ordinary Temperatures and Elevated Pressures.—The attempts of F. W. Pfaff[153] to produce dolomite at ordinary temperatures and elevated pressures are noteworthy in this connection. When a mixture of $CaCO_3$ and anhydrite was subjected to the action of an $MgSO_4$ solution under pressure dolomite rhombohedrons were obtained, but when gypsum was used instead of anhydrite no such reaction took place. Similarly the effect of a solution of $MgCl_2$ and NaCl on powdered anhydrite in the presence of Na_2CO_3 or $(NH_4)_2CO_3$ under pressure was to produce the double carbonate. When the latter

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[153]Neues Jahrb., Beil. Bd. 23, 1907, p. 529.

experiments were repeated, however, they were not always successful and when gypsum was substituted for anhydrite the double carbonate was never obtained.

The influence of $MgSO_4$ on $CaCO_3$ in the presence of NaCl also was tried, and the pressure was held at 100 atmospheres for eight days. The temperature varied from 4° to 14° C. The residue obtained after being treated with a two per cent solution of acetic acid for twenty-four hours analyzed 73.7 per cent of $CaCO_3$ and 26.2 of $MgCO_3$. When the experiment was repeated under the same conditions the residue yielded 80.1 per cent $CaCO_3$ and 20.7 $MgCO_3$.

When he used an apparatus to insure uniform concentration of the $MgSO_4$ and $CaCO_3$ Pfaff obtained, in a similar experiment run for ten days, under a pressure ranging from sixty to eighty atmospheres, at room temperature, a residue which after standing twenty-four hours in a two per cent acetic acid solution, tested as follows: $CaCO_3$ 53.7 per cent, $MgCO_3$ 46 per cent. When the experiment ran one day under the same conditions only 7 per cent of $MgCO_3$ was formed in the residue. Pfaff then endeavored to determine at what pressure the reaction proceeds most favorably, and arrived at the conclusion that at 40 atmospheres the reaction begins, but takes place most quickly at 60 atmospheres and still proceeds even at 200 and 500 atmospheres.

Experiments at Elevated Temperatures and Elevated Pressures.—Of the experiments carried on both at high temperatures and high pressures those of Marignac[154] are among the first. When he heated $CaCO_3$ with a solution of $MgCl_2$ in sealed tubes to 200° C. for six hours there was obtained a product which yielded $CaCO_3$ 48 per cent, and $MgCO_3$ 52 per cent. After only two hours heating, however, the amount of $MgCO_3$ obtained was less.

The experiment of Duroche[155] was also formerly regarded as important in that it seemed to lend support to the volcanic theory of the origin of dolomite. Anhydrous $MgCl_2$ and frag-

[154]Quoted by Hunt, Am. Jour. Sci., 2d ser., Vol. 28, 1859, p. 170.
[155]Compt. Rend., Vol. 33, 1851, p. 64.

ments of porous limestone were heated to dull redness for three hours in a sealed gun barrel. When the fragments were removed they were found to be coated with a scoriaceous mass consisting of $MgCl_2$, $CaCl_2$ and a small quantity of the oxides of Ca, Mg, and Fe. When this was washed off the limestone fragments were found to be partly converted into dolomite.

Later researches by Hoppe-Seyler[156] likewise showed how dolomite might be formed at high temperatures. Thus, he obtained both the double carbonate and magnesite by heating magnesium salts or sea water with $CaCO_3$ in sealed tubes. When $CaCO_3$ was treated with a solution of magnesium bicarbonate and heated to over 100° the same result was obtained.

It will be noted that in the above experiments the pressure was induced only by the effect of high temperature on the reacting substances. In some of Pfaff's experiments,[157] on the other hand, mechanical pressure was applied and the temperature kept lower. The effect of an $MgSO_4$ solution ten times as concentrated as this salt in sea water was tried on $CaCO_3$ at a pressure of sixty atmospheres and a temperature of 40° to 50°. After an interval of six days a residue was obtained which was insoluble in two per cent acetic acid. When the experiment was repeated using $MgCl_2$ instead of $MgSO_4$ the same result was obtained, and an insoluble residue bearing considerable $MgCO_3$ was produced.

Discussion.—In summarizing the experimental data bearing on the alteration theory we find the evidence furnished by experiments carried on at ordinary conditions very conflicting, for while Pfaff and Leitmeier report the production of dolomite artificially under these conditions, all other experimenters have obtained only negative results. As regards Pfaff's experiment in which dolomite was obtained by the action of a solution of $MgSO_4$, $MgCl_2$ and NaCl on anhydrite with the passage of CO_2, it must be admitted that this can have no direct bearing on the formation of extensive dolomite deposits in nature, except in-so-far as it shows the possible production of dolomite at

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[156]Cited by F. W. Clarke, Bull. U. S. Geol. Survey No. 491, p. 537.
[157]Neues Jahrb., Beil. Bd. 23, 1907, p. 529.

ordinary temperature and pressure. The evidence furnished by Leitmeier's experiment, on the other hand, is much more important in this connection. But his results are difficult to understand, since other experimenters have consistently obtained negative results when the same constituents were employed, under almost identical conditions. Even when the magnesium solutions were many times more concentrated than those used by Leitmeier no dolomite was obtained.

In the writer's experiments in which the effect of $MgCl_2$ and $MgSO_4$ was tried on $CaCO_3$ at many concentrations, absolutely no trace of dolomite could be found in the residue when it was tested in the most careful manner with Lemberg's solution. To be sure, small transparent crystals were present which failed to take the stain and which suggested dolomite in several particulars, but these were insoluble even in hot, concentrated acids and the conclusion was forced that they represented quartz grains derived from the corrosion of the glass of the containing flasks. For the present, therefore, it seems best to hold Leitmeier's observations in question. If further work should demonstrate the correctness of his observations, then here we would have valuable data bearing on the possible dolomitization of limestone at ordinary temperature and pressure by a dilute solution of magnesium, and many puzzling features of this process would be explainable.

The high temperature experiments, although they have frequently yielded dolomite, cannot be regarded as having a direct bearing on the problem at hand, as all the evidence goes to show that high temperatures have not prevailed when the great masses of dolomite were formed in nature. The same may be said of the experiments carried on both at elevated temperatures and at elevated pressures. But the data bearing on the production of dolomite at elevated pressures are much more valuable, for in the alteration of limestone to dolomite the pressure of the water column above the scene of the replacement must be taken into consideration. It is conceivable that this has in many cases amounted to several atmospheres. All the evidence, however, is unfavorable to the view that the pres-

sure has amounted in many cases to forty to sixty atmospheres, the pressure at which Pfaff obtained his best results, for there is almost universal agreement that the dolomites are not deep sea deposits.

III. Evidence Bearing on the Leaching Theory.

The power of carbonated waters to remove the lime more rapidly than magnesia from magnesian limestone was first actually demonstrated by Bischof,[158] who after placing the powder of magnesian limestones of known composition in water, passed a stream of CO_2 through the mixture for twenty-four hours. It was found that in case of one of the samples which contained originally 84.57 per cent of $CaCO_3$ and 11.54 of $MgCO_3$ no trace of $MgCO_3$ had been taken into solution.

Almost identical results were obtained by Doelter and Höernes[159] in a similar experiment on a dolomitic limestone from the Wengener formation, which bore 84.82 per cent of $CaCO_3$ and 13.94 of $MgCO_3$. When a powdered sample weighing 2.125 grams was placed in water and a stream of CO_2 passed through for forty-eight hours, the solution contained 0.272 grams of $CaCO_3$ and only a strong trace of $MgCO_3$. In like manner Scheerer,[160] upon exposing the powder of dolomitic limestone containing about 9 per cent of $MgCO_3$ to carbonated water obtained only a trace of $MgCO_3$ in solution, although it was rich in $CaCO_3$.

The experiments of Hardman[161] along this line are important. First a dolomitic limestone from Kilkenny was used. This had the following composition:

		Per cent
$CaCO_3$	....	68.21
$MgCO_3$	....	24.00
$Fe_2O_3 + Al_2O_3$	....	4.32
Silica	....	1.92
$FeCO_3$	....	0.90

110 grains of the crushed limestone were placed in a jar of distilled water and only enough CO_2 passed through to keep

[158]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 195.
[159]Jahrb. K.-k geol. Reichsanstalt, Vol. 25, 1875, p. 328.
[160]Neues Jahrb., 1866, p. 1.
[161]Proc. Roy. Irish Acad., 2d ser., Vol. 2, 1875-77, p. 705.

the water feebly acid. After an interval of seventy-two hours it was found that the carbonates were dissolved in the proportion of 68.21 parts of $CaCO_3$ to 9.32 parts of $MgCO_3$. When, however, the water was saturated with CO_2 for forty-four days the ratio was 68.21 to 20.06. A similar experiment on a limestone from Dungarnon County which bore 12.71 per cent of $MgCO_3$ yielded very similar results.

The experiment of Högbom[162] on a marl from Upsala likewise has an important bearing on the leaching theory. When this marl, which contains approximately 18 per cent of $CaCO_3$ and 1.3 of $MgCO_3$ was treated with carbonated water it was found that almost half of the former was dissolved, while only a trace of the latter was taken into solution.

The effect of carbonated waters on normal dolomite at ordinary pressure, on the other hand, is in general to dissolve the two carbonates with their ratios undisturbed. Thus, when Gorup-Besanez[163] treated dolomite powder with carbonated water for five days the solution contained 55.2 per cent of $CaCO_3$ and 47.7 $MgCO_3$, while the undissolved residue yielded 56.74 per cent $CaCO_3$ and 43.26 $MgCO_3$. When the operation was prolonged over a period of twenty-one days the results were not essentially different. The effect of elevation of pressure, however, appears to be to produce a considerable change in the relative solubility of the two carbonates in dolomite. Skeats[164] is the authority for the statement that "when dolomite is subjected to fresh water containing carbon-dioxide at a pressure of about 5 atmospheres, the magnesium carbonate is dissolved and the calcium carbonate remains almost unaffected."

The effect of dilute acetic acid upon magnesian limestones and dolomite is much the same as that of carbonated water. For instance, Karsten,[165] upon treating with cold dilute acetic acid a sample of the Muschelkalk limestone from the district of Lüneberg which contained 2 to 5 per cent of $MgCO_3$, found that there was left behind a residue which had the composition of normal dolomite. He concluded, therefore, that this rock must

[162]Neues Jahrb., Vol. 1, 1894, p. 266.
[163]Liebig's Annalen, 8th Supp., 1872, p. 230.
[164]Quart. Jour. Geol. Soc. London, Vol. 61, 1905, p. 97.
[165]Quoted by F. W. Pfaff, Neues Jahrb., Beil. Bd. 23, 1907, p. 545.

consist of a mixture of calcite and dolomite. In like manner Forchhammer,[166] upon treating with dilute acetic acid the powder of a dolomitic limestone from Faxö, which contained 16.5 to 17 per cent of $MgCO_3$, found 41.42 per cent of $MgCO_3$ in the residue, while the solution contained 97 per cent of $CaCO_3$ and 3 of $MgCO_3$. The results obtained by Doelter and Höernes[167] by the action of acetic acid on a dolomitic limestone containing 84.82 parts of $CaCO_3$ and 13.94 parts of $MgCO_3$ for forty-eight hours were very similar. The solution contained 91.5 per cent of $CaCO_3$ and 8.5 of $MgCO_3$. But when F. Pfaff[168] employed a more richly dolomitic limestone the enrichment of the residue in $MgCO_3$ was not relatively so great. A dolomite from the French Jura of the Muggendorf region was subjected to the action of a dilute acetic acid solution for twenty-four hours. The original sample consisted of $CaCO_3$ 60.33 per cent, $MgCO_3$ 38.27, insoluble matter 1.40, while the acetic acid solution contained 69.15 per cent of $CaCO_3$ and 30.80 of $MgCO_3$. The residue left behind, however, showed a great enrichment in magnesia, as it bore 40.1 per cent of $CaCO_3$ and 59.8 of $MgCO_3$. Pfaff concluded that this residue must have consisted of a mixture of magnesite and calcite, since the $MgCO_3$ is far in excess of that in normal dolomite.

An elaborate series of experiments by Haushoffer,[169] on the other hand, showed that in the more nearly pure dolomites the $CaCO_3$ does not tend to go into solution more readily than the $MgCO_3$. Indeed, by experimenting with various concentrations of acetic acid and with dolomites of variable composition, he actually found in some cases a slightly higher proportion of $MgCO_3$ in the solution than in the original rock. He gave it as his opinion, therefore, that in normal dolomite the $MgCO_3$ is more soluble than $CaCO_3$ and that the normal order of solubility of the two carbonates is reversed.

[166]Jour. prakt. Chemie, Vol. 49, 1850.
[167]Jahrb. K.-k. geol. Reichsanstalt, Vol. 25, 1875, p. 329.
[168]Quoted by F. W. Pfaff, Neues Jahrb., Beil. Bd. 23, 1907, p. 545.
[169]Quoted by F. W. Pfaff, Idem., p. 547.

FIELD AND CHEMICAL EVIDENCE.

I.   Evidence Bearing on Primary Deposition Theories.

CHEMICAL THEORY.

There are several facts which lend strong support to the view that some stratified dolomites represent chemical precipitates. The more important of these are as follows:

(1) The occurrence of chemically deposited dolomite in veins and druses, etc.

(2) The purity of some stratified dolomites.

(3) The association of dolomite with salt and gypsum deposits.

(4) The interbedding of limestone and dolomite.

(5) The compactness of some dolomites.

(6) The preservation of fine and detailed structures in some dolomites.

(7) The paucity of organic remains in some dolomites.

(8) The great thickness of some dolomites.

(9) The relation of dolomite to limestone in certain formations.

The occurrence of Chemically Deposited Dolomite.—That dolomite can be deposited directly in nature is indicated by its occurrence as a gangue mineral and in veins and druses. The high magnesia-bearing travertines reported by Giradin[170] and by Johnson[171] must likewise represent direct deposits, and occurrences of chemically deposited dolomite on a small scale in dolomitized coral reefs have been reported. Skeats,[172] referring to the latter feature, says:

The lining of calcite-crystals by an outer zone of clear dolomite, described by me as occurring in sections from Mango (one of the Fiji Islands) and also noticed in some of the sections of the Tyrol dolomite described above, is difficult of ex-planation, except on the hypothesis that the dolomite was deposited from solution in optical continuity with the calcite. It sometimes happens that one crystal is built up of successive zones, alternately calcite and dolomite. As these crystals are

[170]See ante, p. 297.
[171]See ante, p. 297.
[172]Quart. Jour. Geol. Soc. London, Vol. 61, 1904, p. 136.

but rarely recognized in thin sections, it is clear that they were not formed under the conditions governing the general dolomitization of the mass of the rock. It may be that they were formed in cavernous parts of the rock, more or less shut off from the free passage of the sea water; and indeed, these crystals are sometimes found lining the walls of cavities. Dr. C. D. Cullis, in the mineralogical report on the Funafuti boring, describes and figures a somewhat analogous case, of the deposition of the two minerals in alternating coats lining the walls of cavities, in a way that simulates on a microscopic scale the appearance of an agate.

Phillipi[173] also states that similar chemically deposited dolomite crystals appear in the dolomitized limestone lumps from the Seine Bank of the Atlantic Ocean northeast of Madeira.

The possibility that dolomite can be formed by direct deposition in nature then must be regarded as proven. But as regards the possible extensive chemical deposition of dolomite beneath the sea either in the past or at the present time we have no positive evidence. To be sure, recent work by Drew[174] has shown that calcium carbonate is being actively deposited through the agency of marine bacteria in the American tropics, but dredging has yet failed to show the presence of dolomitic ooze on the sea bottom.

The Purity of Some Stratified Dolomites.—It has been held by some that certain pure dolomite masses which possess the carbonates of calcium and magnesium in approximately equivalent proportions probably represent chemical deposits rather than alteration products because of their definite composition, and all must agree that this is the simplest explanation of the phenomenon which may be offered. The force of this argument, however, is greatly weakened by the fact that the Niagaran dolomite of the Upper Mississippi Valley which the investigations of the writer have shown to be an undoubted alteration product is, in general, a very pure dolomite, especially in its upper portion, and many analyses show the two carbonates to exist in essentially the same proportion as in normal dolomite.

[173]Neues Jahrb., Festband. 1907. p. 424.
[174]Carnegie Institution of Washington, Publication 182, 1914, p. 9.

Furthermore, ideally pure stratified dolomites are the exception rather than the rule in nature. By far the greater number of dolomites have an indefinite and variable composition.

The Association of Dolomite with Salt and Gypsum Deposits.—Beds of dolomite, as of limestone, frequently occur in association with salt and gypsum deposits, and the impression no doubt lingers in the minds of many geologists that both the dolomite and the limestone so associated have been precipitated chemically, like the salt and the gypsum, during the evaporation of a land-locked sea. Weigelin,[175] in fact, has frankly advocated this method of origin for a dolomite of these relations in West Württemberg. This view is supported by the fact that the dolomite and limestone normally come just below the gypsum, a relationship which we should expect upon the basis of the chemical deposition theory, since these are much less soluble than gypsum and would naturally be the first to be deposited. There can be little doubt that the limestone associated with salt and gypsum deposits is in many cases of chemical origin, and the natural inference from this would be that the dolomite is also. But it must be regarded as possible that a rock deposited originally as limestone under these conditions might later be metamorphosed to dolomite. Ideal conditions for the alteration of limestone would be furnished in evaporating seas where the magnesium salts exist in a concentrated state.

The Interbedding of Limestone and Dolomite.—The simplest and most understandable explanation of the phenomenon of interbedding of limestone and dolomite which suggests itself is found in the primary deposition theory, the limestone and dolomite both being regarded as chemical deposits, and this theory in fact has been adopted by many to account for this relationship. Wagner[176] accepted it for the interbedding in the French Jura, holding that the dolomite constitutes a definite member of the series and is of constant thickness. For the same reason Vogt[177] adopted the chemical theory for certain Norwegian dolomites, and Suess[178] for the interbedded dolomites

[175]See ante, p. 269.
[176]Quoted by F. Pfaff, Pogg. Annalen, 1851, p. 465.
[177]See ante, p. 267.
[178]See ante, p. 267.

of the Plattenkalk. Daly[179] has cited instances of sharp and regular interstratification of limestone and dolomite in the pre-Cambrian of British Columbia and Montana which he regards as strong evidence of the chemical origin not only of these dolomites, but of dolomites in general.

There can be no doubt that the stand of these writers is well taken, but, as will be shown later in this paper, interbedding produced by chemical precipitation of limestone and dolomite, if indeed this be considered a possible method of origin, is not the whole story. In fact, all examples of interbedding examined by the writer are most plausibly explained upon the basis of the clastic deposition and alteration theories. Indeed, in most cases, the evidence in favor of these is positive. It is believed that careful field study of many of these cases of so-called interbedding of limestone and dolomite, especially where the dolomite is relatively free from insoluble matter, would bring out the fact that the dolomite layers do not possess regular, even contacts and constant thicknesses. F. Pfaff[180] long ago showed that Wagner's conclusions regarding the dolomite of the French Jura were erroneous, since this rock fails to constitute a definite member of the series.

The Compactness of Some Dolomites.—Ever since Beaumont[181] pointed out that the alteration of limestone to dolomite should be accompanied by a decrease in volume of 12.1 per cent, there has been a tendency to think of secondary dolomites as vesicular, and the opinion naturally has arisen in the minds of some that compact dolomites are original. Thus, Bischof[182] expresses himself as follows:

The cellular character of dolomite, which, according to Elie de Beaumont and Morlot, results from the replacement of lime by magnesia, is considered to prove that the rock has been altered since its deposition, since otherwise it would be compact. There is at many places compact dolomite, which has, probably, been produced directly.

[179] See ante, p. 269.
[180] Pogg. Annalen, 1851, p. 465.
[181] See ante, p. 286.
[182] Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 159.

Doubtless many advocates of the chemical theory have entertained views similar to those of Bischof. Blackwelder,[183] however, upon finding that the Bighorn dolomite, which he believes in an alteration product, possessed a porosity of only 1.31 per cent, attempted to overcome this obstacle by assuming that the replacement took place in the ooze contemporaneously with deposition.

As far as the writer's experience goes, compactness in dolomites cannot safely be used as a criterion of either chemical deposition or contemporaneous dolomitization, since many dolomites known from their field relations to have been formed by the alteration of limestone subsequent to its deposition show only very slight shrinkage effects. For instance, the dolomitic facies of the Central bowlder bed layer of the Elvins formation, near Elvins, Missouri, has a porosity of only .97 per cent although it contains 16.18 per cent of $MgCO_3$. The pore space of the limestone facies of the same layer amounts to .20 per cent. Again a compact fine-grained limestone from the Saint Louis at Alton, Illinois, has a porosity of 1.3 per cent, while its dolomitized equivalent in the same layer, containing 32.39 per cent of $MgCO_3$, has a pore space of only 4.24 per cent, and many other known secondary dolomites are equally compact. Furthermore, certain dolomites believed to be of clastic origin are very compact. The upper Silurian waterlimes of New York state, which are most satisfactorily explained as clastic deposits, are frequently extremely dense. Compactness, therefore, is not a reliable criterion of origin, and this feature cannot be regarded as favorable to the theory of chemical precipitation of dolomite.

The Preservation of Detailed Structures.—Most dolomites which have been interpreted as secondary after limestone exhibit many signs of obliteration of the original structures of the rock, and the inference naturally follows that the dolomites in which these structures are preserved are primary. Loretz[184] for this reason was led to favor the chemical theory of origin for the dolomites of southern Tyrol, which exhibit fine and

[183]Bull. Geol. Soc. America, Vol. 24, 1913, p. 621.
[184]See ante, p. 266.

detailed structures. Here again, however, the evidence must be regarded as uncertain, since some secondary dolomites still retain these. The Anamosa dolomite of northeastern Iowa, which unquestionably is an alteration product, as shown by its association with dolomitized coral reefs, still frequently preserves fine ribbon stratification along which the rock readily cleaves. Examples of dolomitized corals and other organisms in which the structures are more or less faithfully preserved are also known.

Moreover, dolomites of clastic origin may exhibit no obliteration effects, and these may possess fine stratification. This feature, therefore, cannot be regarded as important in interpreting the history of dolomites.

The Paucity of Organic Remains.—The paucity of organic remains in some of the more ancient dolomites is sometimes postulated as evidence of their chemical deposition under conditions unfavorable to the existence of life, due to the excessive concentration of the sea-water or to some other cause. But it should be pointed out that to advocate this view would be to oppose in a measure the arguments of the strongest supporters of the chemical theory themselves, for $(NH_4)_2CO_3$ generated by the decay of organisms is regarded by them as the precipitating agent of the carbonates of calcium and magnesium entering into the dolomite.

On the whole, this feature cannot be regarded as throwing much light on the problem, since in the first place many of the ancient limestones, low in magnesium, are also nearly barren of fossils, and in the second because in many instances in which fossils were present they were very much obscured, if not wholly obliterated, by the dolomitization of the limestone.

Great Thickness.—Since it seems improbable that the dolomitization of a thick limestone subsequent to its deposition could affect more than the upper portion of the formation, it might be contended that deposits of dolomite aggregating several hundred or even several thousand feet in thickness were laid down directly. Certain of the Cambro-Ordovician dolomites of the Appalachian region are reported to attain a great

thickness and this argument might well apply to them. But if it could be shown that dolomite might be formed by the progressive alteration of limestone during its deposition, this argument would lose much of its weight. Both Skeats[185] and Blackwelder[186] have regarded this method of dolomitization as possible. Thus, Skeats holds that the Schlern dolomite of southern Tyrol, which is 3000 feet thick, and which nearly all agree is a great dolomitized coral reef, was formed by a progressive alteration which kept pace with slow subsidence. The Bighorn dolomite, for which Blackwelder advocates the progressive alteration theory, attains a maximum thickness of 300 feet.

The Relation of Dolomite to Limestone.—Several instances are known where the upper portion of a formation is represented by dolomite and the lower portion by limestone, and this might be interpreted as having resulted from the chemical precipitation of both species, during which the calcium carbonate came down first because of its greater insolubility, and later calcium carbonate and magnesium carbonate mingled were deposited, as the solutions became more concentrated. To Petzholdt[187] this seemed the most plausible explanation of such relations in the Tyrol, but later workers have shown that the dolomites of this region must be regarded as secondary.

Moreover, the evidence is all in favor of the view that the same relations in other formations have been produced by downward dolomitization. In all such examples known to the writer the boundary between the dolomite and the underlying limestone is so wavy and irregular as to preclude the view that the relationship is original.

THE ORGANIC THEORY.

In support of the organic theory of the origin of dolomite several facts may be brought to bear. These are:

1. The existence of dolomitic worm castings and fucoidlike markings in limestones.

2. The occurrence of different faunules in the limestone and dolomite in some cases of interbedding.

[185]See ante, p. 282.
[186]See ante, p. 284.
[187]See ante, p. 265.

3. The power of some organisms to secrete $MgCO_3$.

4. The deposition of $MgCO_3$ through the agency of algae.

Dolomitic Worm Castings and Fucoids in Limestones.—In 1907 Peach and Horne[188] reported the presence of dolomitic worm castings in the Sailmohr and Croisaphuill groups of the Northwest Highlands of Scotland, and suggested that their dolomitic character was due either to the fact that "the worms were selective as to their food or that their gastric juices had the effect of predisposing the casts to be dolomitized under the influence of magnesian solutions more readily than the surrounding mud." Still more recently, R. C. Wallace[189] has described dolomitic fucoid-like markings in certain Ordovician limestones in Manitoba. He was led to conclude after careful study that this relationship had resulted from a process of local replacement produced by the magnesia contained in algae which were imbedded in the limestone at the time it was deposited.

The writer has observed several occurrences of limestones mottled and streaked with dolomitic areas similar to those described by Peach and Horne and by Wallace. But in all of these the phenomenon could be satisfactorily explained only upon the basis of selective dolomitization, since the evidence favored the view that the magnesium was introduced after the limestone was formed. This feature, therefore, cannot be regarded as having a direct bearing on the organic theory of dolomite formation.

Influence of Organisms in the Production of Interbedding.— At least one instance is known where the dolomite and limestone layers of an interbedded series bear different faunules, and this suggests that organisms may have had some influence in the production of this phenomenon. Thus, Von Bibra[190] states that in Franconia marly layers containing as much as 44.8 per cent of $MgCO_3$ and bearing fossil molluscs alternate with unaltered shelly limestone containing on the average only 1.5 per cent of $MgCO_3$ and whose fossil remains consist chiefly of fish.

[188]The Geological Structure of the Northwest Highlands of Scotland: Mem. Geol. Survey Great Britain, 1907, pp. 366 and 379.
[189]See ante, p. 271.
[190]Cited by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 181.

Bischof,[191] in commenting on this occurrence, remarks that "altered conditions of animal life in the ocean appear, therefore, to have taken place during the deposition of these different layers, and this is not opposed to the opinion, that they have been produced by organic action." But after further discussion, the conclusion is reached by him that the high magnesia content of the marly layers has resulted either from leaching out of the lime or from later introduction of magnesia, and this explanation seems most logical. The selective dolomitization of the marly layers might be accounted for readily on the supposition that they were more readily affected than the limestone because of their fine-grained character. It must be regarded as possible also that the organic remains of the marly layers exercised a selective influence during dolomitization.

The Deposition of MgCO₃ through the Agency of Algae.— The power of algae to deposit $CaCO_3$ and to build up deposits of travertine about springs is well known, and that $MgCO_3$ can be deposited with the lime to a limited extent under these circumstances has been shown by the studies of Ludwig and Theobald,[192] but whether such low plant forms have ever actively deposited $MgCO_3$ in the sea to an important extent, as suggested by these investigators, remains an open question. The fact that modern marine calcareous oozes are almost invariably very low in this constituent would suggest that they have not played an important part in dolomite-building. But more evidence is needed on this point.

The Power of Some Organisms to Secrete MgCO₃.—That certain marine organisms have the power of secreting considerable magnesium along with the lime was early shown by Forchhammer[193] and Damour[194]. Högbom[195] in 1894 also emphasized the fact that certain calcareous algae secrete much magnesia. A table of fourteen analyses presented by him shows the composition of a number of species of Lithothamnium collected from many different seas. The $MgCO_3$ content in these ranges from a minimum of 1.95 per cent to a maximum of 13.19, with a general average of 8.17 per cent.

[191]Idem., p. 181.
[192]See ante, p. 270.
[193]See ante, p. 270.
[194]See ante, p. 270.
[195]Neues Jahrb., Vol. 1, 1894, p. 272.

More recently Bütschli[196] has summarized very exhaustively the results of all known analyses of the calcareous skeletons of marine organisms. He found in general that the forms which secrete considerable $MgCO_3$ are those which build calcite skeletons, while the aragonite-secreting forms are rarely found to contain more than 1 per cent of this constituent.

The maximum percentage of $MgCO_3$ for each of the various groups as shown by Bütschli's tables is as follows: Algae 16.99; Protozoa 12.52; Spongiæ 6.84; Octacoralla 9.38; Hexacoralla 0.62; Hydrozoa 0.97; Vermes 7.64; Asteroidea 9.36; Echinoidea 8.53; Holothuroidea 12.10; Bryozoa 4.66; Brachiopoda 3.4; Pelecypoda 1.0; Gastropoda 1.31; Cephalopoda 5.08; Arthopoda 1.38.

Bütschli, as will be observed, does not list any analyses of recent crinoid skeletons, but several such analyses are now on record. Thus, Nichols[197] in 1906, reported 11.72 per cent of $MgCO_3$ in the skeleton of *Metacrinus rodundus* from Japan, and A. H. Clarke[198] shortly after found abundant magnesium in this same species and in one other. A much more elaborate series of analyses of crinoid skeletons, however, are furnished by F. W. Clarke and W. C. Wheeler.[199] All the recent forms analyzed were found to possess a high percentage of magnesia. Thus, the analysis of nineteen species, representing as many genera, collected from widely different localities, which include great variation in depth, temperature, and salinity, showed, when the results were recalculated to eliminate the organic matter, an $MgCO_3$ content ranging from 7.86 to 12.69 per cent. The proportion of magnesium was found to decrease with depth and with decrease in temperature, but the cause of this relation is not known.

The analysis of ten fossil species of crinoids ranging in age from the Lower Ordovician to the Eocene, however, failed to show an important proportion of $MgCO_3$ for all but one. *Encrinus liliiformis* (Lam.) from the Triassic of Braunschweig, Germany, the stem of which bore 20.23 per cent of $MgCO_3$,

[196]Abh. Göttinger Akad, Vol. VI, No. 3, 1908, p. 90.
[197]Field Columbian Museum, Geol. series, Vol. 3, 1906, p. 49.
[198]U. S. Nat. Mus. Proc., Vol. 39, 1911, p. 487.
[199]Prof. Paper U. S. Geol. Survey No. 90D, 1914, p. 33.

yielded less than 3 per cent of this constituent. This contrast in the composition of recent and fossil crinoids is difficult to explain. Clarke and Wheeler state that it is possible that the ancient crinoids were deficient in magnesium, but they believe is more probable that the low magnesium content of these has resulted from loss due to subsequent alteration, "perhaps to the infiltration of calcium carbonate."

A study of the foregoing summary of analyses of marine invertebrates will readily show the inadequacy of these organisms in themselves to build a dolomite. It should be recalled that the magnesium content listed is the maximum one in each case except in the crinoids, and that the great majority of the species of each group show a much smaller amount of this constituent. The rather high magnesium content of some forms then would be greatly diluted in a limestone deposit by the presence of forms low in magnesium. Probably in most cases forms low in magnesium would greatly predominate in a given deposit, but it is well known that certain calcareous algae, such as Lithothamnium, are the principal lime secretors in some modern coral reefs, and it is conceivable that reefs built largely by these forms might bear from the first several per cent of $MgCO_3$.

The possibility that recent crinoids might build a magnesian limestone directly is suggested by the high magnesium content of these. But no evidence has yet been found in support of the view that the Paleozoic crinoids have built such a limestone. Certain horizons in the Burlington and Keokuk limestones of southeastern Iowa are literally filled with crinoid remains, yet these have been shown by analyses made for the writer to be nearly free from magnesium except in the lower portion of the Burlington, which has been dolomitized locally. The accompanying analysis[200] is of a sample of crinoidal Burlington limestone from Morning Sun, Iowa.

	Per cent
SiO_2	2.06
Fe_2O_3	0.64
Al_2O_3	1.62
$CaCO_3$	94.59
$MgCO_3$	1.15

[200]Prof. A. W. Hixson, analyst.

Considering all the evidence, it seems improbable that marine organisms play an important role in dolomite-building in the modern seas, and unless we assume as Nichols[201] has suggested that the Paleozoic forms secreted dolomitic skeletons, we must conclude that they have not played an important role in the past. But Nichols' suggestion has no foundation in fact, since the experience of paleontologists is that unaltered carbonate skeletons of Paleozoic invertebrates consist of calcite and never of dolomite.

THE CLASTIC THEORY.

Several attempts have been made to apply the clastic theory of dolomite formation, and there is some reason for believing that this will hold in certain instances. Some of the facts which lend support to this view are:

1. The intimate association of some dolomites with clastic sediments.

2. The high siliceous and argillaceous content of some dolomites.

3. The calcareous fossils and thin seams of limestone included in some impure dolomites show no signs of alteration.

4. The lack of obliteration and shrinkage effects in some dolomites.

5. The interbedding of limestone and dolomite.

The Association of Dolomite with Clastic Sediments.—When dolomite is intimately associated with sandstone and shale, which are both clastic, the assumption might be made that the dolomite also is clastic. Phillipi[202] has advocated this method of origin for certain dolomite beds associated with clastic sediments in the Muschelkalk of Germany. But this is, from the nature of the case, difficult to prove, since it might be contended also that such dolomites represent chemical deposits, or have resulted from the alteration of limestone. As regards the first of these possibilities, it is difficult to conceive of dolomite being deposited chemically under these conditions. But there

[201]See ante, p. 271.
[202]See ante, p. 274.

could be no valid objection to the last contention. Indeed, the writer has found thin layers of dolomite in the Warsaw shales at Warsaw, Illinois, which must be secondary, as shown by the fact that they locally grade laterally into limestone only partly if at all dolomitized. Moreover, some of the best known examples of dolomites, examples which exhibit many of the characteristics of clastic deposits, are not associated with sandstone or shale but rather with limestone.

When, however, the dolomite associated with shale and sandstone is impure and is seen to merge laterally into shale or into pure limestone showing no alteration effects, the evidence of its clastic origin is much stronger. Certain impure dolomitic limestones in the Keokuk formation of southeastern Iowa exhibit these relations and are believed for this as well as other reasons to represent clastic deposits.

High Siliceous and Argillaceous Content. Since it is believed by those who uphold the clastic theory that the dolomitic sediments are derived from the residuum of older limestones, we should expect clastic dolomites to be high not only in magnesia, but also in insoluble impurities. But high siliceous and argillaceous content in dolomites is in itself not a reliable indication of their clastic origin, since many limestones also are high in these constituents, and dolomitization of these would give rise to an impure dolomite. Moreover, in many instances silica has been introduced into dolomites subsequently to their formation, and this must always be taken into account. This criterion, therefore, can be used safely only in conjunction with several others.

Unaltered Fossils and Thin Limestone Seams.—In all examples known to the writer in which fragments of calcareous fossils and thin limestone seams appear in dolomites of known secondary origin, these invariably show signs of corrosion or of imperfect dolomitization. When, therefore, these are well preserved in dolomite and show no signs of alteration even under the microscope, the conclusion is at once suggested that the latter are original. This would apply especially well in the case of those dolomites which are impure and grade locally into

clastic sediments. Certain dolomitic limestones of the Keokuk formation of southeastern Iowa exhibit all these relationships.

Lack of Obliteration and Shrinkage Effects.—That these features cannot be applied indiscriminately in interpreting the history of dolomites has been pointed out. Some dolomites known to be secondary after limestone locally show little or no trace of obliteration and shrinkage effects, but it is seldom that a secondary dolomite exhibits these features either throughout its thickness or over wide areas. When they are consistently wanting, therefore, some support is lent to the view that the dolomite is primary, but even then this criterion should be employed guardedly, since it has not been disproven that some stratified dolomites are primary chemical precipitates. But where dolomites exhibit several other features suggestive of their clastic origin, the absence of obliteration and shrinkage phenomena must be regarded as lending still stronger evidence of their having been formed in this manner.

The Interbedding of Limestone and Dolomite.—As previously shown, the interbedding of limestone and dolomite is most easily explained upon the basis of primary difference in the materials deposited, and many geologists who have expressed themselves on this subject have adopted the chemical theory as furnishing the most satisfactory explanation of the phenomenon. But Lesley[203] has advocated the clastic theory of origin for the interbedded series of limestone and dolomite in the "Calciferous" near Harrisburg, Pennsylvania, and Grabau[204] holds that it will apply in many cases of interbedding.

Regarding the value of this criterion, the experience of the writer is that it should be applied with care, since selective dolomitization and related phenomena may give rise to a pseudo-interbedding of limestone and dolomite which can be distinguished from true interbedding only by careful study. For instance the interbedding of limestone and dolomite described by Lesley as existing in the "Calciferous" appears to have resulted entirely from dolomitization. This is clearly indicated

[203]See ante, p. 272.
[204]Principles of Stratigraphy, 1913, p. 760.

by the fact that some of the dolomite layers pass abruptly into limestone when followed along the dip, and by the fact that many of the interbedded layers of limestone are mottled and streaked with patches of dolomite. Furthermore, the boundaries of the dolomite layers frequently do not coincide with the bedding planes, but are wavy and undulating.

It must also be regarded as possible that some cases of interbedding have resulted from progressive dolomitization of certain beds during deposition. The dolomite of the ''Lower Buff Beds'' of the Upper Mississippi Valley was doubtless formed in this manner. This member of the Platteville maintains a thickness of approximately fifteen feet over hundreds of square miles and is directly overlain by compact limestones. That it represents an alteration product is clearly indicated by the occasional presence of small remnants of limestone within its mass.

It must also be regarded as possible that some interbedded limestones and dolomites represent chemical deposits, and for this reason also interbedding is not a reliable indication of clastic deposition. When, however, the dolomite layers bear considerable siliceous impurity and grade laterally into shale on the one hand and into limestone on the other by transitional stages in which interfingering is developed, the evidence is strongly in favor of their being clastic. Especially is this true if fossil fragments and thin limestone seams in the dolomite show no signs of alteration under the microscope. There are several examples known to the writer which exhibit these relations. The most notable of these is found in the Keokuk formation at Keokuk, Iowa. At two horizons in the section, separated by an interval of about twenty-five feet, beds of ash-colored, fine-grained, siliceous, dolomitic limestone appear. The lowermost of these averages about six feet in thickness, while the upper one is about fifteen feet thick. The remarkable geodes for which this locality is famous come mainly from these two beds.

The results of an incomplete analysis of the upper bed made by the writer are given below.

	Per cent
Insoluble matter	33.8
Fe_2O_3 and Al_2O_3	2.8
$CaCO_3$	39.99
$MgCO_3$	12.50
Moisture and carbonaceous matter	7.70
Undetermined	3.21
	100.00

In general these dolomitic members of the Keokuk maintain their individuality over wide areas, and the upper member is traceable over an area several hundred square miles in extent. But locally they merge wholly or in part into argillaceous shale or fossiliferous limestone, and the transitions are characterized by an intimate interfingering of the shale and dolomitic limestone on the one hand and fossiliferous limestone and unfossiliferous dolomitic limestone on the other. The transition into pure limestone is entirely a physical one resulting from original differences in sedimentation, since not the slightest evidence of dolomitization is to be found in the limestone.

Very nearly the same relations as described above are shown by the Warsaw formation in Ste. Genevieve county, Missouri. This formation attains a thickness of approximately 120 feet in this region, and the upper one-half consists of fine-grained, impure, siliceous, dolomitic limestone, with a few rare, thin layers of bluish, coarse-grained, fossiliferous limestone in the upper portion. An exposure in the west bluff of the Mississippi river one mile below Clement, Missouri, exhibits the character of this portion clearly. The succession here is as follows:

	Feet	Inches
Limestone, gray, medium-grained, slightly oölitic; the lowermost portion of the Salem (exposed)	5 ±	
Limestone, soft, buff, impure, dolomitic, contact with bed above regular and even, no fossils noted	5	10
Limestone, gray, medium-grained, fossiliferous, weathering into thin layers	2	3
Limestone, soft, buff, impure, dolomitic, no fossils noted	5	8
Limestone, gray, medium-grained, rather thinly bedded, fossiliferous	2	9
Limestone, ash-colored, fine-grained, impure, dolomitic, sparsely fossiliferous	31	6
Clay, soft, plastic, weathering yellowish, fossiliferous	6	

The pure limestone layers are sharply and regularly inter-
bedded with the dolomitic ones over wide areas, and show no
trace of alteration. Furthermore, the calcareous fossils of
the dolomite are perfectly preserved.

The Upper Silurian waterlimes of New York state also ex-
hibit many of the earmarks of clastic deposits and Grabau[205]
in fact has advocated their clastic origin. These waterlimes
consist of dark, fine-grained, compact, siliceous, dolomitic lime-
stones bearing on the average 20 to 25 per cent of $MgCO_3$. In
the eastern part of the state these waterlimes are interbedded
with gray, compact, fossiliferous limestones, and yet the con-
tacts are sharp and regular and continuous over wide areas.
These interbedding relations are excellently shown in the region
about Rosendale, where the waterlimes were formerly exten-
sively quarried for the manufacture of natural cement.

II. Evidence Bearing on the Alteration Theories.

The field evidence furnishes a mass of data favorable to
the alteration theories of the origin of dolomite, but it will
not in itself always indicate the conditions under which the
alteration was effected. Thus, it is not possible to say in all
cases whether the dolomitization took place while the limestone
was still beneath the sea, through the agency of sea water, or
after its emergence, through the agency of ground water. The
evidence which may be introduced in favor of the alteration
theories may be classified first, as that inherent in the dolo-
mites themselves, and second, that based on the association of
limestone and dolomite.

Inherent Evidence.

    (1)   Dolomite pseudomorphs after calcite.
    (2)   The great range in composition of the stratified
           dolomites.
    (3)   Dolomitized coral reefs.
    (4)   Dolomitized fossils in dolomites.
    (5)   Dolomitized oölites.
    (6)   Obliteration and shrinkage effects.

[205]Bull. Geol. Soc. America, Vol. 24, 1913, p. 399.

(7) The association of gypsum with some dolomites.

Evidence Based on the Association of Limestone and Dolomite.

(8) Vein dolomites.
(9) Mottled limestones.
(10) Remnants of limestone in dolomite.
(11) Nests of dolomite in limestone.
(12) Irregular contacts of limestone and dolomite.
(13) The lateral gradation of dolomite into limestone.
(14) Pseudo-interstratification effects.

INHERENT EVIDENCE.

Dolomite Pseudomorphs.—Dolomite pseudomorphs after calcite are not uncommon. Several occurrences of such pseudomorphs were reported long ago by Blum[206] and many more have since been described by Haidinger[207] and others. These can only have been formed by the substitution of $MgCO_3$ for a portion of the $CaCO_3$ of calcite crystals. Here, then, the validity of the alteration theory is established, and the replacement of limestone by magnesia on a much larger scale must be regarded as not only possible but highly probable.

Range in Composition.—As has been shown, there is every gradation in the $MgCO_3$ content of limestone, from pure limestone free from this constituent, on the one hand, to dolomite with an excess of $MgCO_3$ on the other (see Table II, p. 260). This great range in composition surely would not characterize a chemical deposit, nor can it be satisfactorily explained upon the basis of the clastic or leaching theories, because of the freedom of most dolomitic limestones from considerable insoluble impurities. When we consider that the alteration theory will allow all degrees of replacement of limestone by magnesia the phenomenon is readily explainable. The variable composition of the dolomitic limestones as a whole, therefore speaks strongly for their secondary origin.

Dolomitized Coral Reefs.—The existence of both recent and fossil dolomitized coral reefs indicates the possible operation

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[206]Cited by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 165.
[207]Trans. Roy. Soc. Edinburgh, 1827, p. 36.

of dolomitization on a large scale. Many examples of recent
or near recent dolomitized coral reefs exist in the coral islands
of the southern Pacific as shown by the work of Dana,[208]
Skeats,[209] and others, and Branner[210] has reported the presence
of a dolomitic reef rock in the old stone reefs of Brazil. These
can have resulted only from the alteration of the calcareous
skeletons of corals and other organisms of the reef. When,
therefore, dolomitized coral reefs are found in the ancient dolo-
mites, these dolomites can have had no other than a secondary
origin. The most notable examples of fossil coral reefs now
represented by dolomite are found in the Niagaran of Iowa
and Wisconsin and in the great Schlern dolomite of Southern
Tyrol.

Dolomitized Fossils.—When fossils which are known to have
been originally calcareous are found to be represented by dolo-
mite in dolomitic formations it is difficult to avoid the conclu-
sion that these formations have resulted from the replacement
of limestone. Instances where the skeletons of organisms are
replaced by dolomite are not common, since the fossils are
usually represented by molds in dolomites. The problematic
fossil Cryptozoan, however, has been found to be represented
by dolomite in several instances. In the Shakopee dolomite of
the Upper Mississippi Valley dolomitized remains of this or-
ganism are sometimes met with. They have likewise been
observed in the Allentown dolomite near Allentown, Pennsyl-
vania; in the Little Falls dolomite at Little Falls, New York;
and in the Joachim dolomite near Bloomsdale, Missouri. Dolo-
mitized corals are also occasionally found in dolomites. These
are not uncommon in certain dolomite beds of the Cedar Valley
limestone at Fairport, Iowa, and they appear also in the Lock-
port dolomite at Niagara Falls, New York.

Altered Oölites.—It has been our experience that calcareous
oölites, when formed, consist of pure, or nearly pure calcium
carbonate. Where, therefore, oölite beds in the midst of dolo-
mite formations are composed of dolomite, the inference is
that both the dolomitic oölite and the rock inclosing it have

[208]Am. Jour. Sci., Vol. 45, 1843, p. 120.
[209]Bull. Mus. Comp. Zoöl., Vol. 42, 1903, p. 53.
[210]Idem., Vol. 44, 1904, p. 265.

resulted from dolomitization, and where the oölite is only partly changed to dolomite, and so shows unquestionably that it was originally calcareous, the evidence in favor of dolomitization must be regarded as positive. In the course of the writer's studies several oölites have been found in the midst of dolomites, and strangely enough, these have been for the most part only partly altered, although the inclosing rock is uniformly dolomitized. The details of the alteration of these oölites will be considered in the section on the petrographic evidence.

Imperfectly altered oölite beds occurring in association with dolomite are found in the Elbrook limestone at West Waynesboro, Pennsylvania; in the Elvins formation at Elvins, Missouri; in the Allentown limestone near South Bethlehem, Pennsylvania; in the Hoyt limestone near Saratoga Springs, New York; in the basal portion of the Oneota dolomite at McGregor, Iowa; in the Tribes Hill limestone at Canajoharie, New York; and in the Monroe dolomites near Sylvania, Ohio.

Obliteration and Shrinkage Effects.—The massive and all but structureless character of some dolomites has frequently been remarked upon, and there can be little doubt that in many instances this massive character was taken on at the time of dolomitization, as the bedding planes of the original thinly-bedded limestone were largely obliterated by the welding which accompanied the recrystallization induced by dolomitization. Thus, in the Galena limestone of Clayton county, Iowa, which has suffered dolomitization locally, the limestone facies is thinly and distinctly stratified, but the dolomitic facies is heavily bedded and the thick massive layers are separated by faint planes which are often indistinctly shown even on weathered surfaces. The limestone and dolomite facies of the Niagaran in Delaware county, Iowa, exhibit similar differences.

The obliteration of structures seems to have taken place typically where the dolomitization was accompanied by shrinkage, i. e., where the alteration proceeded by molecular rather than by volume replacement. Where the replacement is truly molecular the transformation of limestone to dolomite should be accompanied by a decrease in volume of about 12.1 per cent

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as pointed out by Beaumont.[211] Few of the massive dolomites which are known to be secondary probably show as much shrinkage as this, but some of them are very vesicular and it is in these that the structures are most obliterated.

While indications of obliteration of structures and of shrinkage furnish good evidence of the secondary origin of the dolomites which exhibit them, it cannot be argued conversely that compact dolomites which exhibit no obliteration effects are original, for the replacement may sometimes take place after the law of equal volumes as enunciated by Lindgren,[212] as shown by the fact that certain dolomites known from their field relations to be secondary after limestone fail to exhibit these features. One of the most notable examples of this method of replacement is found in the Saint Louis limestone of southeastern Iowa. Freshly exposed surfaces of the dolomitic facies of this formation are frequently nearly or quite as thinly bedded as the limestone facies and no evidence of shrinkage is to be seen. The Allentown dolomite in the region about Allentown, Pennsylvania, also shows little or no sign of obliteration of structures or of shrinkage, yet its secondary origin is suggested by the fact that it contains both dolomitized oölites and skeletons of Cryptozoan.

Some of the well known dolomites in which the writer has observed obliteration and shrinkage phenomena are: the Leithsville dolomite at Allentown, Pennsylvania; the Oneota and Shakopee dolomites of the Upper Mississippi Valley; the Little Falls dolomite of the Mohawk Valley, New York; the Galena, Fort Atkinson, and Niagaran dolomites of northeastern Iowa; the Bonneterre, Doerun, Derby and Potosi dolomites of the Ozark region; the Monroe dolomites of Michigan and Ohio; the Cedar Valley dolomites of eastern Iowa; and the Spergen dolomites of southeastern Iowa and eastern Illinois.

The Association of Gypsum and Dolomite.—When gypsum is found occupying small pockets and filling shrinkage vugs in dolomite the suggestion at once comes to mind that this gypsum represents a reaction product of dolomitization and was pro

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[211]See ante, p. 286.
[212]Econ. Geol., Vol. 7, 1912, p. 521.

duced by the action of $MgSO_4$ on limestone. Absolute proof of this is wanting, of course, since the exact time of the introduction of the gypsum cannot be determined. As a criterion of origin, then, the value of this feature cannot be emphasized strongly. But taken in conjunction with other features it may serve to strengthen the evidence.

Examples of gypsum occurring in association with dolomite are not common, and the only case met with by the writer was found in the Lockport dolomite of the Niagara Falls region. Morlot,[213] however, has described several other instances where dolomite and gypsum appear in intimate association.

EVIDENCE BASED ON THE ASSOCIATION OF LIMESTONE AND DOLOMITE.

Vein Dolomites.—The development of dolomite along fissures in limestone furnishes positive evidence in favor of the alteration theory, provided no signs of extensive leaching are shown. Probably most vein dolomites have been produced through the agency of ground water circulating along the fissures, but there is not general agreement on this point.

Vein dolomites are of common occurrence in the Lahn district as pointed out by Klipstein,[214] who early reported that in this region the dolomite not only traverses the limestone as distinct veins or dikes, but also is imbedded in it as nests and large irregular masses. Similar phenomena were later described by Grandjean[215] from the lower Lahn district. According to him the dolomite is developed here to the greatest extent where the limestone is most subject to the penetration of water.

Other vein dolomites have been described in the same general region by Von Strombeck and by Abich. Bischof[216] summarizes their observations as follows:

Dyke-shaped masses of dolomite, generally in a vertical position, were also observed in limestone by v. Strombeck and Abich at the Kahlen-Berg, near Echte, between Göttingen and Brunswick, and in the valley of Tramonte. At several places near

[213]Haidinger's Naturw. Abh., Vol. 1, 1847, p. 305.
[214]Cited by Bischof, Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 185.
[215]Cited by Bischof, Idem., p. 193.
[216]Idem., p. 185.

the Lahn the dolomite intersects the limestone strata and spreads out over them like a roof six or eight feet thick. In some of these dikes the dolomite is very much decomposed and presents a striking contrast with the unaltered limestone adjoining.

Similarly Harkness[217] has described cases where dolomite appears to follow joints in the Carboniferous limestones in the district about Cork, Ireland. Local masses of dolomite in the limestone here assume courses in intimate agreement with the direction of the joints. "In some instances the line of the joint, when the joint is closed, forms the boundary between the dolomite and the ordinary limestone; the two distinct portions terminating abruptly against the sides of the joint." Harkness concluded that the jointing was antecedent to dolomitization, but believed the alteration to have been effected by sea water.

Vein dolomites have also been reported in the Carboniferous limestones of South Wales.[218] In the country around Abergavenny dolomitization is closely associated with faults, and the alteration effects die out on each side of these. It is suggested that waters from the Coal Measures which are known to be high in magnesium and barium salts are responsible both for these dolomites and for the associated joints and crack infillings of barytes.

Dixon[219] likewise states that vein dolomites following fissures are of frequent occurrence in the Carboniferous limestone along the coast of South Wales between Mumbles Head and Pwlldu. These were formed subsequent to pre-Triassic deformation, and are regarded as of Triassic age, and to have been caused by the downward percolation of water from the surface. The more continuous beds of dolomite in the formation must have been produced prior to the disturbance. These he interprets as contemporaneous. The vein dolomites may be distinguished from the contemporaneous ones by the fact that they show "(1) larger average size and greater clearness of the rhombo-

[217]Quart. Jour. Geol. Soc. London, Vol. 15, 1858, p. 86.

[218]Strahon and Gibson and others. The Geology of the South Wales Coal Fields, Part 2; Mem. Geol. Survey, England and Wales, p. 33.

[219]The Geology of the South Wales Coal Field, Part 8; Mem. Geol. Survey, England and Wales, 1907, p. 16.

hedra; (2) the inclusion of hematite; (3) the association with calcification; (4) the preference of dolomitization for oöliths and corals.''

Whatever uncertainty may be entertained regarding the origin of the foregoing vein dolomites, no doubt need exist regarding the manner of formation of those closely associated with ore deposits. These can have been formed only through the agency of ground water. Several such occurrences have been described. For instance, Bischof,[220] quoting Coquand, states "that where the auriferous quartz veins of the gold mine La Gardette, extend from the gneiss into the Lias limestone, the latter is converted into black dolomite and bears auriferous galena; but, at a distance of a few centimeters, it is quite free from magnesia.''

Local dolomitization is also associated with the lead and zinc deposits of the Joplin district.[221] "The ores are invariably connected with dolomite either fresh or rotten, and reach sidewise into the limestone only as far as the latter is dolomitic and crystalline.'' Somewhat related features are described by Spurr,[222] who states that dolomite follows fractures and faults in the upper part of the Leadville formation in the Aspen district, Colorado. The dolomitization effects gradually die out on each side of the fissures, as shown by analyses. Dolomitization is associated with the ore here as at Joplin. Spurr states that "the local dolomitization invariably accompanies the ore. Even when the latter is in blue limestone there is usually a sort of envelope of dolomite around it, which in turn is surrounded by limestone.'' These vein dolomites cannot be distinguished from the associated contemporaneous dolomites microscopically, according to him. It would appear, therefore, that Dixon's observations will not apply generally. The origin of the Aspen vein dolomites is ascribed to the action of hot springs such as those which still exist at Glenwood Springs nearby and which, according to his observations, are producing similar dolomitization effects today. More recently Michael[223]

[220]Elements of Chemical and Physical Geology, English translation. Vol. 3, 1859, p. 180.
[221]Schmidt, A., Trans. St. Louis Acad. Sci., Vol. 3; No. 2, 1875, p. 246.
[222]Mono. U. S. Geol. Survey, Vol. 31, 1898, p. 208, ff.
[223]Zeitschr. Deutsch. geol. Gesell. Prot., Vol. 56, 1904, p. 127.

has shown that dolomitization has followed closely certain lines of disturbance in the Muschelkalk beds near Tarnowitz and elsewhere. The phenomenon is closely associated with mineralization here also, and the conclusion is reached that the alteration has been accomplished by ground water through the introduction of $MgCO_3$ and the removal of $CaCO_3$.

Mottled Limestones.—Within recent years several occurrences of limestone mottled with patches of dolomite have been described and commented upon. These mottled limestones are of two general types, viz.: (1) those in which the dolomite patches follow worm castings or fucoid-like markings, and (2) those in which the dolomite patches exhibit irregular shapes and relations and show no guiding influence. These types of mottling will be referred to as organic and inorganic respectively. Some attempt has been made to explain the first type, but the last has been only briefly mentioned.

Dolomitic worm castings have been described by Peach and Horne[224] from the Croisaphuill group of the Northwest Highlands of Scotland. Their description is as follows:

Towards the base the beds consist chiefly of massive beds of dark grey limestone full of worm castings, which are now chiefly represented by dolomite, so that they stand out in mottled masses on the weathered surface of the rock, the limestone matrix having yielded to solution more readily than the dolomite. Such rocks are highly fossiliferous, but where bands of granular dolomite make their appearance fossils are rarely met with. The middle portion is made up chiefly of unfossiliferous granular leaden-colored dolomite with a few light colored bands of limestone full of worm casts. The upper part, consisting of massive sheets of fossiliferous limestone full of worm casts preserved in dolomite, resembles the lower subdivision.

Worm castings are also reported by these writers[225] to occur in the underlying Sailmohr group. But this rock is uniformly dolomitic, and is described as a massive, crystalline, granular dolomite charged with dark worm castings in a grey matrix, and known locally as the "leopard stone." The view enter-

[224]The Geological Structure of the Northwest Highlands of Scotland: Mem. Geol. Survey, Great Britain, 1907, p. 379.
[225]Idem., p. 366.

tained by these writers as to the origin of the dolomitic worm castings is made clear by the following quotation:

Thus up to the very top of the Cambrian series of Sutherland and Ross impressive evidence is supplied by the abundance of worm casts that the rocks must have accumulated in the state of fine mud or ooze, probably derived mainly from the minute organisms of the plankton. The fact that the worm casts in the two upper groups of the series are for the most part preserved in dolomite while the matrix remains a limestone, suggests that either the worms were selective as to their food or that their gastric juices had the effect of predisposing the casts to be dolomitized under the influence of magnesian solutions more readily than the surrounding material.

R. C. Wallace,[226] in a recent paper entitled "Pseudobrecciation in Ordovician Limestones in Manitoba," also has described dolomitic markings suggestive of organisms in limestones. The succession of formations involved there is as follows:

	Feet
Stony Mountain formation	190
Upper mottled limestone	130
Cat Head limestone (dolomitic)	70
Lower mottled limestone	70
Winnipeg sandstone	100

The dolomitic markings manifest themselves as irregularly distributed darker areas which have their greatest linear extent along the bedding planes, where they exhibit a branching structure. They are characterized by a content of iron as well as of magnesia which is higher than that of the limestone, and with the exception of a few large shells are free from the fossil fragments so numerous in the latter rock. Separate analyses of the dolomite and limestone areas yielded Wallace the following results:

	LIGHT COLORED	DARK COLORED
	PER CENT	PER CENT
SiO_2	1.56	1.56
Total iron as Fe_2O_3	0.16	1.94
(FeO	0.12	0.45)
Al_2O_3	0.06	2.27
$CaCO_3$	94.02	71.03
$MgCO_3$	4.33	23.35
Total	100.13	100.15

[226]Jour. Geol., Vol. 21, 1913, p. 402.

As is shown by the following statement, the view is entertained by Wallace that the mottling has resulted from alteration:

A study of the margin of the darker areas leaves no doubt that we are dealing with secondary dolomitization. Although there is a definite marginal line, it shows so sharp interpenetration of dolomitized and undolomitized material that it could have been caused only by the irregular advance of waters bearing magnesian salts in solution.

After carefully reviewing the whole subject of mottling, however, the conclusion is reached that algæ imbedded in the rocks are responsible for the phenomenon, thus:

There remains the hypothesis that the mottling is connected with algic decomposition. Analyses due to Goedechens show that the percentage of MgO in the ash of algæ collected from the west coast of Scotland may reach 11.66. If, then, the algæ of the sea bottom became buried under a thin coating of calcareous ooze before actual decomposition ensued, the liberated Mg salts might, in conjunction with the sea water of fairly high Mg content, cause such increase of Mg ions locally as to give rise to actual dolomitization. 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 dolomitization. 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. Again, thin sections of the dolomitized areas occasionally show a narrow central tube of clear, well crystallized calcite, indicating that a cavity had existed when the dolomitization took place and that this was subsequently infilled with calcite. Such cavities might be formed when, owing to decomposition, the organism disappeared. The hematite and limonite of the recrystallized dolomitic material would be attributed to the iron salts of the algæ.

It will be noted that Wallace emphasizes the importance of algæ as contributors of magnesia to the dolomitizing solutions and there can be no doubt that certain algæ do contain considerable magnesia in their tissues. It does not seem probable

to the writer, however, that this constituent would ever attain the proportion sufficient to dolomitize the surrounding limestone to such a marked degree.

The data obtained in the course of the writer's studies lead him to adopt an alternative hypothesis of origin for both the organic and inorganic types of mottling. All cases of mottling examined seem to be best explained on the assumption that the magnesia was introduced from without and that the mottling has resulted from the selective replacement of fucoids in the one case and from the spreading out of the alteration from certain favorable centers in the rock in the other. Consistent with this view are the following facts:

(1) The existence of unaltered fucoid-markings containing less than two per cent of $MgCO_3$ in association with dolomitic ones.

(2) The association of both types of mottling with dolomite seams and other evidences of imperfect dolomitization.

(3) The gradation of mottled beds into beds which are uniformly dolomitic, both laterally and vertically.

(4) The existence of every gradation between limestone showing incipient mottling and true dolomite.

Thus it appears that mottling represents merely an incipient stage in the process of dolomitization, and it is believed that many dolomites have passed through such a stage in the progress of their formation. Here, then, we have a clue to the origin of all those masses of dolomite with which such mottling is associated.

EXAMPLES OF MOTTLED LIMESTONES.

Many examples of mottled limestones associated with dolomite have been met with in the course of this investigation. These will be described as far as possible in the order of their geologic age.

The Elbrook Formation.—The limestones of the Elbrook formation are commonly uniformly dolomitic, but mottled limestones occur at several horizons in the vicinity of Waynesboro, Pennsylvania. A hand specimen, in the writer's collection, from the quarry located in the southwestern portion of the town, consists of fine-grained dark gray limestone with irregular wavy seams of fine-grained, lighter gray dolomite ranging from about 1 mm. to 12 mm. in thickness. These are approximately parallel to the stratification of the rock, but some of them extend across the stratification planes and invade the adjacent limestone layers. Under the microscope the dolomite seams are shown to possess no definite contact lines, but to grade gradually into the limestone through transitional stages.

Elvins Formation.—The Davis member of the Elvins group, of southeastern Missouri, exhibits mottling on a large scale. This member attains a thickness of approximately 170 feet according to the measurements of Buckley,[227] and is both overlain and underlain by extensive dolomite formations. Excellent facilities for studying these beds are afforded in the cuts of the Illinois Southern Railroad between the stations of Flat River and Elvins. The upper sixty-three feet of the formation as developed here consists of dolomitic shales and limestones, while the remaining portion, with the exception of twenty-five feet of dolomite at the base, is only imperfectly altered. In this part the thinly bedded limestones are streaked and blotched with buff dolomite. The dolomite patches follow no definite pattern, but typically form discontinuous streaks along the stratification planes and irregular areas within the limestone layers. At many points the alteration has proceeded so far that only small irregular remnants of limestone entirely surrounded by dolomite remain. It seems probable that this mottled character was taken on by the Davis member at the time the overlying dolomites were formed, and that the dolomitizing solutions not only were weakened by reaction with the limestone above, but also were hindered in their circulation by the more impervious shaly beds in the upper portion of this member.

[227]Mo. Bur. Geol. and Mines, Vol. 9, part 1, 1908, p. 38.

The Beekmantown Limestone.—An excellent exhibition of mottling is shown by the limestones associated with dolomite in the Tribes Hill member of the Beekmantown as it is developed in the Mohawk Valley of New York state. Unusually good opportunity for studying the mottled stone of this formation is furnished in the abandoned quarries at Canajoharie and at Palatine Bridge.

By previous observers the significance of the mottled character of some of these beds seems not to have been appreciated and the coarser-grained dolomitic patches have almost invariably been described as consisting of arenaceous material.

As regards the details of the mottling, two main types may be recognized. These are: first, a mottling produced by the dolomitization of the limestone in an irregular and imperfect manner by alteration along stratification lines and in irregular patches; and, second, a mottling produced by a more regular and selective dolomitization along well directed lines and apparently following fucoid markings in the limestone. In the latter type, the dolomite forms more or less cylindrical, branching pipes running indiscriminately through the limestone but having their greatest linear extent along the bedding planes. The original outline of these, however, has been obscured in a number of instances by the spreading out of the dolomitization from them into the adjacent limestone. At some points both types of mottling are developed in the same layer and there a network of dolomite streaks appears. In both types the local alteration has been accompanied by increase in size of grain and in both the dolomitic areas tend to stand out in relief as yellowish patches on weathered surfaces of the gray limestone.

The relations of the mottled limestone are well shown in a large abandoned quarry situated about one-half mile west of the station of Palatine Bridge along the New York Central and Hudson River railroad. The following section was measured at the east end of the opening:

		FEET	INCHES

7. Limestone, conglomeratic, showing no visible signs of alteration 2–3

6. Dolomite, brownish 3

5. Limestone, gray, compact, with dolomitic fucoid markings....   8

4. Limestone, dove-colored, compact; upper two-thirds with occasional discontinuous seams of dolomite; lower one-third with dolomitic fucoid markings.................. 9

3. Dolomite, brownish, bearing fucoid markings of a darker tint, and resembling the "leopard stone"................ 3–4

2. Limestone, gray, compact, with dolomitic fucoid markings, grading up into the dolomite above through a transition zone 2 to 3 inches thick................................   8

1. Limestone, gray, compact, grading up into the mottled rock above (exposed) 2

The contact of No. 3 with the bed below is fairly sharp and regular, but the contact with the bed above is much less regular, for near the middle of the quarry face the dolomite bed thickens greatly, mainly at the expense of the mottled zone in the lower part of No. 4. Thus, No. 3 and No. 4 are each six and one-half feet thick here and the mottled zone at the base of No. 4 is reduced from three feet to one foot.

Samples of the mottled limestone, and of the uniformly dolomitized rock from bed No. 3 have been analyzed by Prof. A. W. Hixson. The dolomitic and non-dolomitic areas of the mottled limestone were tested separately.

	LIMESTONE AREA	DOLOMITE AREA	DOLOMITE
	PER CENT	PER CENT	PER CENT
SiO_2	2.90	9.28	2.82
Fe_2O_3	1.43	5.00	3.14
Al_2O_3	3.87	7.28	6.40
$CaCO_3$	84.49	62.73	55.62
$MgCO_3$	5.81	15.01	32.60
Total	98.50	99.30	100.58

Similar relations of mottled limestone to dolomite are shown in the quarries at Canajoharie. In a small quarry a short distance west of the village a layer of dolomite eighteen inches thick, overlain and underlain by mottled limestone, grades laterally into mottled limestone itself. This relationship is

again shown in an abandoned quarry in the eastern part of Canajoharie. At the top of this quarry there appears a bed of mottled limestone six feet in thickness bounded above and below by thin layers of conglomeratic and slightly oölitic limestone which shows only incipient alteration of the matrix. Now the lower two feet of this mottled limestone member grades locally into a uniformly dolomitic rock through a transition zone only a few inches in extent. The gradation is accompanied by a gradual spreading out and enlargement of the dolomitic patches until they finally coalesce. Every stage, therefore, may be traced between a limestone with dolomitic fucoid markings to a uniform dolomite. There can be no escape from the conclusion that this mottled limestone represents an incipient stage in the process of dolomitization.

Precisely the same sort of mottling is developed in division D of the Beekmantown in the Lake Champlain region. A fine exposure of these mottled beds appears in the escarpment below the walls of old Fort Ticonderoga. The succession here from above downwards is approximately as follows:

		FEET	INCHES
6.	Dolomite, dark gray, faint traces of fucoid markings showing on weathered surfaces; upper portion bearing seams and reticulations of chert	12	
5.	Concealed	7	
4.	Limestone with pipes and reticulations of dolomite which stand out in relief on weathered surfaces..............	4	4
3.	Dolomite, dark gray, with thin siliceous seams..............	2	8
2.	Limestone, gray, fine-grained, with dolomitic fucoid markings	2	6
1.	Dolomite, dark gray, showing fucoid markings on weathered surfaces; some layers cherty, the chert following fracture lines, stratification lines, and to some extent the fucoid markings. Exposed	20	

The limestone beds here, in addition to bearing dolomitized fucoids, also bear numerous dolomitized tests of Ophileta and Orthoceras, although the limestone matrix immediately adjacent is little if at all affected. Dolomite bed No. 1, which exhibits traces of fucoid markings, doubtless itself passed through a mottled stage during its formation comparable to that now exhibited by beds No. 2 and No. 4, but for some unknown reason it was altered more completely and more uniformly.

Other occurrences of mottled limestone, mainly of the fucoidal type, in association with dolomite, appear in divisions A and B of the Beekmantown at Shoreham, Vermont; in the Coplay limestone of Beekmantown age near Catasauqua, Pennsylvania; and in the Beekmantown at Staufferstown and at Harrisburg, Pennsylvania.

The Chazy Limestone.—Mottling of both the organic and the inorganic types appears in the Chazy limestone in the Lake Champlain region. The fucoidal mottling is well developed in the limestone exposed near Shoreham, Vermont. An outcrop in a small hillock on the east side of the road about one-half mile north of Shoreham shows dolomitic fucoid-markings at several horizons, and in the higher beds the tests of Maclurea also are dolomitized. The matrix of the dolomite areas seems to be but little affected, and the original outlines of the fucoid markings are well preserved. At one horizon in the lower beds dolomitization of the fucoids has been very imperfect and many of the markings are still preserved in an unaltered condition. These are of a darker tint than the limestone and can be distinguished from it with little difficulty. In order to determine if possible the cause of the selective dolomitization of such fucoid markings, samples of the darker areas and of the limestone matrix were submitted to Mr. H. F. Gardner of Columbia University for analysis. After the moisture and carbonaceous material were eliminated by heating, the following results were obtained.

	LIGHT COLORED PER CENT	DARK COLORED PER CENT
SiO_2	0.52	0.56
$Al_2O_3 + Fe_2O_3$	1.04	0.52
$CaCO_3$....................................	97.50	97.36
$MgCO_3$	0.98	1.18
Total..........................	100.04	99.62

It will be noted that the $MgCO_3$ content of the fucoids is not appreciably greater than that of the limestone, and this constituent could not have exerted much selective influence. Nor do the analyses afford any other clue to the problem.

Microscopic examination of the darker material in thin section failed to reveal the presence of organic structures, but it is filled with dark inclusions which doubtless consist of organic matter. It seems probable that the selective dolomitization may be attributed largely to this, for reasons which will be considered later.

On Valcour Island also, in Lake Champlain, mottling is extensively developed in the Chazy, but here it is predominantly of the inorganic type. In all of the divisions of the formation exposed here the limestone is almost universally mottled on a small scale with areas of buff dolomite. Commonly the dolomite appears in the form of irregular streaks and patches along the stratification lines, but in many cases it forms small irregular areas scattered through the limestone layers. In most instances these dolomite areas are notably finer-grained than the limestone. Especially is this true of the areas in the coarse-grained fossiliferous limestones. This has resulted from the breaking down of the large calcite grains and fossil fragments into aggregates of fine dolomite grains during the alteration, a phenomenon which accompanies the alteration of all coarse-grained limestones. Moreover, the dolomite areas in the Chazy are in general softer and less resistant than the coarse-grained limestone and seldom stand out in relief as do the dolomite areas in the fine-grained limestones of the Beekmantown.

No beds of limestone within the Chazy, as developed here, were found to be uniformly dolomitized, but Brainard and Seeley[228] report that a dolomitic limestone member caps the formation at the north end of the island.

The Plattin Limestone.—Mottling is developed on a small scale, locally at least, in the basal portion of the Plattin limestone of the Ozark region. The mottled limestone constitutes a transition bed from the uniformly dolomitic Joachim limestone below to the unaltered compact limestones of the Plattin above. An unusually good opportunity for studying these relations is found in a small quarry opening about one and one-half

[228]Bull. Am. Mus. Nat. Hist. Vol. 8, 1896, p. 306.

miles north of Perryville, Missouri, in a large sink-hole just
west of the McBride road. The following section appears at
this point:

FEET INCHES

PLATTIN:

Shale, buff, calcareous, with thin layers of compact gray
    limestone 8   6
Limestone, dark gray, compact, with irregular seams and
    patches of lighter gray dolomite which weather yellowish 4
Limestone, gray, imperfectly dolomitized, forming abrupt
    transition from dolomite below to mottled limestone
    above   1

JOACHIM:

Dolomite, bluish when fresh but weathering yellowish,
    heavily bedded 5   6

The dolomite patches of the mottled limestone member are
irregular in shape, and although for the most part they attain
their greatest linear extent along the bedding planes of the
rock, they are not confined to these, for a number of tongue-like
extensions of the dolomite areas shoot out short distances into
the limestone.

The Galena Limestone.—Mottling of the inorganic type is
excellently developed in the Galena limestone at several lo-
calities in Clayton county, Iowa, as was first pointed out by
Leonard,[229] who speaks of the mottled limestone as "partially
dolomitized beds" and states that they constitute transition
beds between the dolomitic and non-dolomitic portions of the
formation. Incomplete analyses of the limestone and dolomite
areas of the rock which were made for him showed them to con-
tain 4.31 and 18.28 per cent of $MgCO_3$ respectively.

In rare instances the mottled limestone does not occur at the
contact of the dolomite and limestone facies, but is developed
farther down with several feet of limestone intervening. But
typically the mottled rock forms a transition from the dolo-
mite above to the limestone below. Therefore since the contact
of the limestone and dolomite facies is not a definite plane but
wanders up and down in the formation, the mottled limestone
appears at no definite horizon.

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[229] Ia. Geol. Survey, Vol XVI, 1905, p. 250.

The mottled limestones of the Galena attain their greatest known development in the west bluff of the Mississippi river back of the town of Guttenberg, Iowa. The succession of beds in the Galena as measured and described by the writer is as follows:

FEET

4. Dolomite, buff, vesicular, becoming pitted on weathered surfaces, grading abruptly into the bed below 65
3. Limestone, gray fine-grained, mottled with patches of buff dolomite which become smaller and more distant in the lower beds; in layers from 2 inches to 1 foot in thickness; with locally developed dolomite beds in middle portion 90
2. Shale, bluish, argillaceous 1
1. Limestone, gray, slightly argillaceous, no mottling noted. Exposed.... 35

Thirty-five feet above the base of No. 3 there appears a ledge of buff dolomite four to five feet thick. Above this comes five to six feet of mottled limestone, and then six to seven feet of dolomite again. When these layers of dolomite were traced laterally along the bluff for a distance of about ten rods, they were found to pass, in part, into mottled limestone, but never were the dolomite beds found to disappear entirely. Thus, at the north end of the section the upper bed is split into two almost equal parts by two feet of mottled limestone. The dolomite patches in No. 3 do not appear to increase notably in size either at the contact with No. 4 or in the vicinity of the dolomite layers within the member itself, but where the dolomite layers grade laterally into mottled limestone there is a gradual transition in the size of dolomite areas, from a dolomite with subordinate limestone areas to limestone with subordinate dolomite areas.

Attention should be called to the fact that no mottling appears below the shale layer No. 2 and that the number and size of the dolomite patches in the lower part of No. 3 decreases downwards. This would seem to indicate that the dolomitization here was a descending process and that the mottling was developed by imperfect alteration at the time the overlying limestones were uniformly altered.

As regards the details of the mottling of the Galena, it may be said that the dolomite areas possess no constant shape or

23

size; that they are very irregular in outline; and that they possess no structure which would suggest the original presence of fucoids in the limestone. They are buff in color, coarser-grained than the gray limestone areas, and are essentially free from fossil remains, owing to the obliteration of structures which accompanied the dolomitization. Their boundaries appear to be fairly definite megascopically, but when examined under the microscope they are found to be gradational, dolomite rhombohedrons being disseminated in the limestone several millimeters beyond the main dolomite areas.

The Maquoketa Formation.—The Elgin limestone member of the Maquoketa formation shows a mottled structure locally in the neighborhood of Ft. Atkinson, Iowa. In a small exposure below the bridge over Turkey river one mile east of the town, the phenomenon is unusually well shown. About fifteen feet of the limestone is exposed here in the east bluff of the stream. The upper three or four feet is quite shaly, consisting of shale with nodular layers of limestone. The lower portion, however, consists of fairly pure calcareous layers. Originally this limestone was dense, gray and unaltered, but now it is mottled with patches and irregular seams of buff dolomitic limestone. Between layers of dolomitic limestone containing remnants of unaltered limestone on the one hand and layers of gray limestone containing seams and patches of dolomitic limestone on the other, every gradation is shown here.

The Hamilton Limestone.—Mottled limestone associated with dolomite appears in the Hamilton limestones in a bluff along the Toledo, Peoria and St. Louis railroad, about two miles above Chautauqua, Illinois. A bed of dolomite eight feet in thickness appears in the limestone at this place, and within this bed, one to two feet above its base, a zone of mottled limestone eight inches thick is locally developed. In the dolomite itself crinoid stems and brachiopods are still preserved as calcite. Many of the limestones interbedded with dolomite in the Middle Devonian of Iowa are also frequently blotched with dolomite. This relationship is well exhibited in the exposures at and near the town of Fairport, in Muscatine county.

The Louisiana Limestone.—Mottled beds have been observed in this limestone both at the type section at Louisiana, Missouri, and in equivalent beds of the Kinderhook group at Burlington, Iowa. At Louisiana the mottling appears in an irregular transition zone ten feet or more in thickness between a uniformly dolomitic limestone above and unaltered limestone below. The dolomitic areas of the mottled rock are medium-grained in texture and brownish in color, while the limestone areas consist of compact, gray, lithographic stone.

The relations at Louisiana are well shown in the bluff exposures at the foot of Tennessee Street and along Edison Avenue. The succession here from above downwards is as follows:

	FEET	INCHES
HANNIBAL:		
Shales, bluish, argillaceous	25±	
LOUISIANA:		
Limestone, buff to brownish, medium-grained, dolomitic, lower boundary indefinite	25±	
Limestone, mottled gray and brownish, gradually passing into the dolomite above by increase in size of brownish areas, and into the limestone below by increase in size of gray areas	10±	
Limestone, light gray, lithographic, breaking with conchoidal fracture	10±	
CHATTANOOGA:		
Shale, bluish, calcareous	1	
Shale, black, fissile	3–4	
Shale, bluish, argillaceous		3
Sandstone, yellowish, fine-grained, soft		3
Disconformity.		
ALEXANDRIAN:		
Limestone, brownish, dolomitic	3	
Limestone, gray, oölitic	7	
Disconformity.		
MAQUOKETA:		
Shale, bluish, calcareous, exposed	3	

It seems clear from the relations shown here that the dolomitization of the upper portion of the Louisiana and the formation of the mottled beds took place in the closing stages

of Louisiana time prior to the deposition of the Hannibal shale and that the process of alteration proceeded from above downwards. This view is supported by the fact that the impervious nature of the Hannibal shale above would prevent sufficient ground-water circulation to accomplish dolomitization subsequent to its deposition and by the fact that the intensity of the transformation dies out downwards. Moreover, the dolomitization is in no way related to secondary structures, such as joints in the limestone.

In the Burlington section of the Kinderhook group a thin limestone member which retains all the characteristics of the typical Louisiana also exhibits mottling. This member ranges from eleven to eighteen feet in thickness and is both overlain and underlain by fine-grained, yellowish calcareous sandstone. It consists typically of light gray, thin-bedded, dense, lithographic limestone, but in places it is partly dolomitized and exhibits thin seams of yellowish coarser-grained dolomite along the bedding planes and irregular patches within the layers. At certain points the horizontal seams unite with the interior patches and the dolomite areas assume a reticulated appearance. Small remnants of limestone are in such cases entirely enveloped by dolomite.

In the Nagel quarries located in the bluff of the Mississippi river about two miles below Burlington the bed attains a thickness of eleven feet and consists of three feet of uniformly dolomitic limestone in its upper portion, with eight feet of mottled limestone below. Dolomite seams are greatly extended along the bedding planes of the mottled portion, and some of them are traceable for a distance of several feet.

The Saint Louis Limestone.—One of the best illustrations of mottling in the Saint Louis is found along Potter's Branch, a small creek which enters the Des Moines river from the northeast about one mile below Bonaparte, Iowa. About three-fourths of a mile back from the river badly fractured and very imperfectly dolomitized limestone appears along the bed of the branch. The fracture lines have been healed with calcite, and curiously enough the limestone in the immediate vicinity of the

calcite veinlets is unaltered and where the fracture lines are closely spaced the limestone is either free from dolomite or only mottled with it, while the limestone surrounding the areas of local disturbance is everywhere dolomitic. The mottling developed here, then, represents imperfect dolomitization under unfavorable conditions.

The Main Limestone.—According to Dixon,[230] mottled limestones occur in the Main limestone member of the Carboniferous of South Wales, but their relation to the dolomite beds of the formation is not made clear. The mottling characterizes one horizon and has been observed at several localities. It is referred to as "pseudo-brecciated" structure by Dixon, who points out that the relations are original and not due to crushing. His analyses of the limestone and dolomite areas of the "pseudo-breccia" showed them to vary widely in their magnesia content. These are given below:

	LIGHT COLORED PER CENT	DARK COLORED PER CENT
SiO_2	5.85	2.22
H_2O at 105° C.............................	.21	.06
Fe_2O_3, etc.	.63	.25
CaO	34.17	50.98
MgO	15.29	3.21
CO_2	43.60	43.62
Total...........................	99.75	100.54

Remnants of Limestone in Dolomite.—The presence of local areas of unaltered limestone surrounded on all sides by dolomite in a given formation speaks unequivocally in favor of the view that the dolomite has resulted from the alteration of limestone. But remnants of limestone in dolomite seem to be the exception rather than the rule, and this criterion seldom can be applied in interpreting the history of dolomites.

Limestone remnants in dolomite have been observed by the writer in division B of the Beekmantown near Shoreham, Vermont. In the upper portion of this division there is a bed of

[230] The Geology of the South Wales Coal-field, part 8; Mem. Geol. Survey, England and Wales, 1907, p. 10.

compact gray dolomite with an exposed thickness of ten feet which contains irregular areas of finer-grained, dark gray limestone several inches across. These have no definite shape or relations and many of them are penetrated by seams of dolomite.

In the Niagaran dolomite of Delaware and Buchanan counties, Iowa, limestone remnants are developed on a much larger scale, as pointed out by Calvin[231] and verified by the writer. With reference to the limestone remnants in Delaware county Calvin says:

A very unusual phase of the Niagara limestone is seen at a few points in Union township. A fine-grained, bluish, compact limestone, not dolomitic, and resembling some portions of the Devonian, occurs in small patches a few yards in extent. These patches were supposed at first to be Devonian outliers, but their relations to the ordinary granular Niagara dolomite, into which they grade laterally and which sometimes overlies them, preclude their reference to the Devonian. One of the best examples of the phase described occurs a short distance west of the southeast corner of section 8 in the township named. Another patch of the same kind occurs near the northeast corner of the same section. More of the same stone is found one-fourth mile north of the center of section 19, and it is shown in an instructive exposure along the north line of section 29. Masses of the blue, fine-grained limestone lie in the midst of granular dolomite and are portions of continuous layers that, except in non-dolomitized spots, possess the characteristics of the ordinary Niagara. All the exposures named are purely local phenomena, small patches of Niagara that in some way escaped the process of dolomitization.

More extensive non-dolomitized portions of Niagara limestone occur in Coffins Grove township. All the beds through a thickness of 20 or 30 feet and over an area some miles in extent, are non-dolomitic. Some of the beds are quite fossiliferous, the fossils being chiefly corals; and while the corals elsewhere at this horizon are usually silicified, they are here unchanged except by the interstitial deposition of calcite. Typical exposures of the beds under consideration are seen near the center of section 26 in the township named, and the same beds crop out

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[231] Ia. Geol. Survey, Vol. 8, 1897, pp. 154 and 218.

in the bluff along Prairie creek in section 28. The beds may be satisfactorily studied in the low bank of the creek at the point where the stream is crossed by the Masonville road, in the northwest quarter of section 28. . . .

The limestone remnant in the Niagaran in Buchanan county appears in section 2 of Hazelton township where coarse granular dolomite passes beneath fine-grained non-dolomitized limestone which may possibly represent the horizon of the evenly bedded quarry stone (dolomite) in the upper parts of the Delaware stage in Delaware and Jones counties.

Nests of Dolomite in Limestone.—As Bischof[232] has pointed out, the occurrence of nests of dolomite in limestone can be accounted for only on the basis of dolomitization. Several such occurrences are known. Klipstein[233] reported the presence of dolomite nests in the "transition" limestones of the Lahn district in 1843, and within recent years Salomon[234] has described nests and tongues of dolomite in the Ladinic limestones of the Alps. Again R. A. Smith[235] reports the presence of nests and large chimney-like masses of nearly pure dolomite in the coral limestone of the Traverse group at Alpena, Michigan.

The writer also has observed several instances where nests of dolomite appear in limestone. Thus, in the upper portion of the Saint Louis limestone at Alton, Illinois, bowlder-like masses and irregular lenses of dolomite are extensively developed. In the quarries which have been opened in the east bluff of the Mississippi river a short distance above the town there appears a thin-bedded, fine-grained, compact gray limestone three feet in thickness, which bears rounded masses of darker gray, coarser-grained dolomite ranging from a few inches up to six feet in greatest diameter (see figure 33). They normally lie with their longest diameter approximately parallel to the stratification and are in some places thickly set in the limestone, but elsewhere none appear within a horizontal interval of fifty feet or more. These dolomite masses at first glance might be taken

[232]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 187.
[233]Quoted by Bischof, idem, p. 185.
[234]Abh. K.-k. geol. Reichsanstalt, Vol. 21, Part I, 1908, p. 408.
[235]Private communication.

FIG. 33. Bowlder-like masses of dolomite in Saint Louis limestone at Alton, Illinois.

for true bowlders, but careful study shows them to have been
formed in place by the local dolomitization of the limestone.
This is clearly indicated by the fact that the contact of the
bowlders with the limestone matrix is in some instances grada-
tional, and that the stratification lines of the limestone else-
where may be traced directly through the bowlders. Analyses
of a sample of the limestone and of one of the bowlders by
Prof. A. W. Hixson yielded the following results:

	LIMESTONE PER CENT	DOLOMITE PER CENT
SiO_2	2.90	4.78
Fe_2O_3	1.14	1.93
Al_2O_3	.66	3.97
$CaCO_3$	91.88	57.41
$MgCO_3$	3.39	32.39
Total	99.97	100.48

In a bed of limestone a few feet above the bowlder bed irregu-
lar lenses and thin discontinuous layers of dolomite of the same
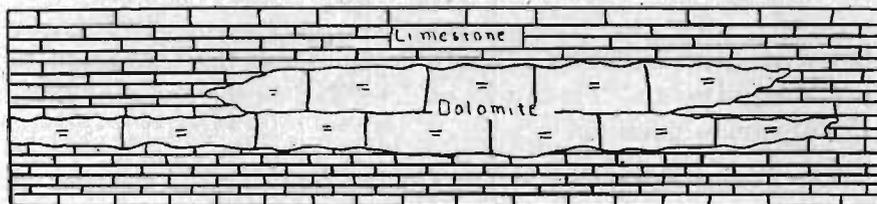physical character are developed (see figure 34).

FIG. 34.   Irregular lens of dolomite in Saint Louis limestone at Alton, Illinois.   Scale, one inch=eight feet.

Similar lenses and bowlder-like masses of dolomite occur on a less extensive scale in the Saint Louis limestone along Indian creek near Farmington, Iowa, and in the Spergen limestone near Belfast, Iowa.

Lateral Gradation of Dolomite into Limestone.—Since it is not conceivable that dolomite could be deposited at one point and limestone at another only a short distance away, the lateral gradation of dolomite into limestone must be regarded as furnishing unimpeachable proof of the secondary origin of all dolomites showing these relations. Such a gradation was described long ago by Daubeny,[236] who stated that at Lake Lugano, in northern Italy, a limestone at one point is destitute of magnesium, farther along the lake it is traversed by small veins of dolomite, and still farther on it contains crystals of the same in small cavities, and finally it passes into dolomite with the disappearance of all traces of stratification.

Hardman[237] also has described instances of the lateral gradation of dolomite into limestone in the Carboniferous limestones of Ireland. Thus:

It is frequent also in the county Kilkenny in many places within a circle extending from Gowran to near Ballyrogget, and I have hand specimens showing the gradual alteration, the fossils being completely obliterated, and the blue limestone at one side becoming perfectly crystalline dolomite on the other. Large masses of dolomite are seen which when traced out abut against and merge into limestone, and in some places, as at Ballyfayle, there will be as many as twenty or more alternations of limestone and dolomite in a distance of less than half a mile, the limestone always full of marine fossils, by no means dwarfed in appearance.

[236]A Description of Active and Extinct Volcanoes, 2d ed., 1848, p. 150.
[237]Proc. Roy. Irish Acad., 2d ser., Vol 2 (Science), 1875-77, p. 728.

Many examples of lateral gradation have been observed by the writer, in limestone ranging in age from the Cambrian to the Mississippian. These will be described in the order of their stratigraphic position.

The Elvins Formation.—The Central bowlder bed member of the Elvins formation exhibits such relations repeatedly in a cut of the Illinois Southern Railroad between Flat River and Elvins, Missouri. This bed, although it is overlain by shaly beds and underlain by impure mottled limestone, consists typically of very pure light gray, fine-grained, compact limestone in the form of large bowlders imbedded in a shaly matrix, but locally it forms a continuous bed for several yards, and there it is apt to be imperfectly dolomitized. Large irregular patches of dark gray dolomite several feet across commonly appear in it, and at one point the bed is altered completely from top to bottom for a distance of several yards. A comparison of the analyses of the pure limestone facies of this bed as given by Buckley[238] with the analysis of the dolomitic facies made by Prof. A. W. Hixson for the writer will show the marked difference in the magnesia content of the two varieties.

	LIMESTONE FACIES		DOLOMITIC FACIES
	1	2	
SiO_2	2.43	5.31	6.42
Fe_2O_3			3.35
Al_2O_3	0.80	0.69	7.81
$CaCO_3$	94.00	93.00	64.87
$MgCO_3$	2.94	0.23	16.18
Moisture	0.10	0.05	....
Total	100.27	99.28	98.63

The porosity of the limestone facies is .20 per cent while that of the dolomitic facies amounts to .97 per cent.[239]

The Platteville Limestone.—Lateral gradation of dolomite into limestone is also illustrated by the "Lower Blue Beds," a limestone member of the Platteville formation as developed in

[238]Mo. Bur. Geol. and Mines. Vol. 9, Part I, 1908, p. 43.
[239]Determinations by Prof. A. W. Hixson.

the Upper Mississippi Valley lead region. At Dubuque, and at all other localities in Iowa, where this member is exposed, it consists of bluish, fine-grained, thin-bedded limestone about twenty feet in thickness, and is followed above by the Decorah shale member and below by the dolomitic limestones of the Lower Buff Beds. But at Darlington, Wisconsin, very different conditions are met. Here the member is uniformly dolomitized, as mentioned by Bain[240] and verified by the writer, and is followed directly by the dolomitic limestones of the Galena. On fresh surfaces the dolomite assumes a massive appearance very unlike the thin-bedded, non-dolomitic facies in Iowa.

The Fayette Breccia.—This phenomenon is exhibited to a lesser degree by the Fayette breccia in Linn county, Iowa, and this, together with other features, has given rise to some misapprehension as to the true nature of the Siluro-Devonian contact in Iowa.

In his report on the geology of Linn county, Norton[241] recognizes the following succession of formations:

Devonian (Wapsipinicon)	Upper Davenport Lower Davenport	} =Fayette breccia
	Kenwood	
	Otis	
Silurian	Coggan	
	Bertram	
	Anamosa	
	LeClaire	
	Delaware	

In a later report on the geology of Cedar county, the same writer[242] concluded that the Coggan should be referred to the Wapsipinicon, but no further reference to the Bertram was made.

[240]Bull. U. S. Geol. Survey No. 294, 1906, p. 24.
[241]Ia. Geol. Survey, Vol. IV, 1894, p. 127.
[242]Ia. Geol. Survey, Vol. XI, 1900, p. 320.

The Bertram formation has its typical development "along Big creek and its tributaries from Springville and Paralta to Bertram." It is described as medium to light drab in color, as compact in texture, as sub-conchoidal in fracture, as magnesian in composition, and as locally exhibiting brecciation. At one point an exposure shows it resting directly on the Anamosa and this fact, together with its lithologic character, seems to be the sole basis for referring it to a horizon below the Coggan.

The preliminary studies of the writer lead him to suggest that the Bertram beds really represent a local dolomitic facies of the Fayette breccia let down on the Anamosa by discon-formity, due to the Kenwood and Otis beds being cut out here. This interpretation is borne out by the facts that the so-called Bertram is locally non-dolomitic along Big creek, and that it then resembles the Fayette breccia in every particular. More-over, evidence of a disconformity below the Fayette breccia has been observed in the cut of the Chicago, Milwaukee and St. Paul Railroad a short distance west of the station at Fayette, Iowa, where the breccia rests very irregularly on the surface of the Otis.

The Spergen Limestone.—Similar occurrences of dolomite grading laterally into limestone are found in the Spergen lime-stone in southeastern Iowa. This formation has been very im-perfectly dolomitized, and some beds which are dolomitic at one point are represented by limestone only a few rods, or at the most, only a few miles, away. This feature is remarkably well shown in certain outcrops of the formation near Belfast, Iowa. The limestone has a most confusing way of grading laterally into dolomite, utterly different lithologically, within short dis-tances and to one not familiar with true conditions the relations are very baffling to say the least. The unaltered facies consists of light gray, thin-bedded, coarse-grained crinoidal limestone, while the dolomitic facies is buff, fine-grained, massive and vesicular. The relations are still further complicated by the tendency of the limestone not only to pass into dolomite litho-logically different, but also to grade abruptly into fine-grained, bluish, calcareous sandstone.

One of the best illustrations known to the writer of the lateral gradation of dolomite into limestone in the Spergen at this locality is found in an old quarry face along the Chicago, Rock Island and Pacific railway three-fourths mile south of Belfast. The relations here are exhibited by the accompanying sketch (figure 35).

FIG. 35. Showing relations of dolomite to limestone at one point in quarry face, three-fourths mile south of Belfast, Iowa. Scale, one inch=twelve feet.

The Saint Louis Limestone.—Lateral gradation is exhibited along with other phenomena of imperfect dolomitization in the Saint Louis limestone of southeastern Iowa. This formation is dolomitic throughout in some sections, while in others nearby only certain layers are dolomitic. This has been clearly demonstrated by detailed study of the formation as developed along the Des Moines river in Lee and Van Buren counties. The faunal zones were worked out carefully here, and were traced from section to section. A great variation in the nature and degree of dolomitization was demonstrated. For instance, at one locality the formation was dolomitic from top to bottom, at another it was predominantly dolomitic, although a few layers of limestone still persisted, while at still another point the dolomite was subordinate and limited to thin zones. Thus, the dolomite is confined to no definite horizon, and the relations are very irregular and inconstant.

Frequently the dolomitization of the Saint Louis has been influenced somewhat by its structure. Thus many of the reef-like masses of disturbed and broken limestone which are common in this formation are but little if at all altered, while in

many cases the undisturbed limestones on their flanks are uniformly dolomitic. This must be interpreted as meaning that dolomitization took place after the reef-like masses were formed. An instructive illustration of the influence of such structures on the dolomitization of the Saint Louis is found in the face of an abandoned quarry in the northeast bluff of the Des Moines river a short distance above the mouth of Reed creek, two miles southeast of Bonaparte, Iowa (see figure 36).
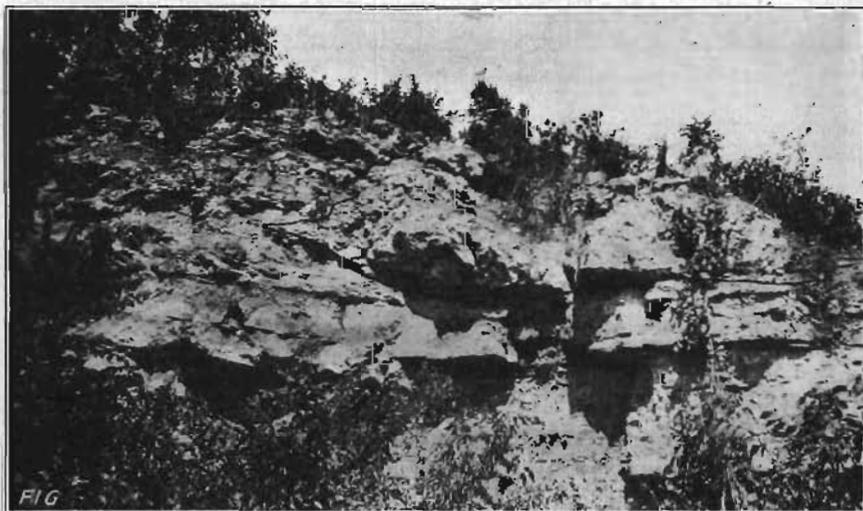
FIG. 36. Reef of unaltered, brecciated limestone bounded below and on the flank with undisturbed dolomitized limestone. Abandoned quarry above mouth of Reed creek, two miles southeast of Bonaparte, Iowa.

Irregular Boundaries.—Examples are known where limestone formations are dolomitic either in their upper or lower portions only and in these the boundary between the two divisions is sometimes very irregular and wavy. Such relations can have resulted only from the partial dolomitization of a formation originally represented entirely by limestone.

EXAMPLES OF IRREGULAR BOUNDARIES.

The Galena Limestone.—Probably the most striking boundary relations known in any dolomite are shown by the dolomitic facies of the Galena formation in northeastern Iowa. In the region about Dubuque the Galena is dolomitic from top to

bottom, and is represented by massive beds of buff, sparsely fossiliferous dolomitic limestone. To the northward, however, the lower portion of the dolomite tends to pass into limestone to a variable degree, thus giving rise to a very irregular lower boundary for the dolomite. At Specht's Ferry, nine miles north of Dubuque, twenty-five feet of limestone, with intercalated shaly layers in the upper portion, intervenes between the Decorah shales and the dolomite, while at Guttenberg, in Clayton county, twenty-five miles northwest of Dubuque, 125 feet of limestone, the upper 90 feet of which is mottled with dolomite, occupies the same position.

At Clayton, on the other hand, which lies only eight miles north of Guttenberg, only fifteen feet of limestone capped by a shale bed two feet in thickness, separates the dolomite from the Decorah shales. Still more striking relations are exhibited at other localities in Clayton county, as was pointed out by Leonard.[243]

In section 14 of Wagner township, non-magnesian strata have an exposed thickness of seventy-five feet and are seen to be overlain by the Maquoketa shales. Between six and seven miles to the south and at the same horizon the dolomitic beds are found at Elkader, with a thickness of at least 120 feet. At Volga the strata lying immediately beneath the Maquoketa are non-dolomitic, and along the Turkey river in Marion township similar beds are exposed at many points in the same position. At Osborne, only a little over four miles east of Volga, eighty feet of heavily bedded dolomite are exposed just below the shales of the Maquoketa.

Thus it is seen that the boundary relations between the limestone and dolomite facies of the Galena are very irregular and what is thin-bedded fossiliferous limestone at one locality is represented by massive dolomite at another only a few miles away. This confusing relationship was formerly the cause of much misapprehension regarding the true nature of the Galena. In the early geological reports on the region the dolomite and limestone facies were referred to two distinct formations, and the dolomite was called Galena while the unaltered limestones, locally present in the lower part of the formation, were included

[243]Ia. Geol. Survey, Vol. XVI, 1905, pp. 248 and 249.

in the formation now designated the Platteville, and were called Trenton. N. H. Winchell,[244] however, basing his argument on paleontological evidence, concluded that the two facies were formationally identical and Calvin[245] soon after verified this conclusion by field study. Calvin's views on the subject are presented below.

As above stated, the unchanged beds have been called Trenton, the dolomitic beds Galena; and the apparently irreconcilable statements concerning the thickness of the respective assumed formations have been due to the preconception that the whole of the Galena overlies the whole of the Trenton, with a definite formational or stratigraphic plane of separation between them. Instead, a large part of the Galena near Dubuque is the exact equivalent, bed for bed, of a correspondingly large part of the Trenton in northern Iowa. Bands characterized by distinct types of life run parallel and continuously through dolomite in one place and unaltered limestone in another. . . . The line of separation is not formational; it pays no regard to stratigraphic planes, except that in places it seems to be determined for some distance by beds of shale; it cuts across individual layers and life zones in the most erratic manner; and while, on the whole, it rises towards the north, it wanders up and down through many feet in very short space, as evidenced by the sections recorded by Hall near Elkader, Clayton City, and Guttenberg in Clayton county.

It looks as if dolomitization had affected the limestone and produced the Galena type after the formation was complete; that the process began at the top and progressed downwards; and that the depth to which the change descended was in some instances and to some extent at least, determined by the presence or absence of impervious beds of shale.

With Professor Calvin's interpretation of the conditions existing here the writer is in complete accord. There seems to be no escape from the conclusion that the present relationship has resulted from a process of dolomitization which began at the top of the formation and proceeded downwards at the close of deposition, or at least in the closing stages. To the northward the alteration was less complete and more sporadic than to the southward where the transformation was more vigorous

[244]American Geologist, Vol. 15, 1895, p. 33.
[245]Ia. Geol. Survey, Vol. X, 1899, p. 406 ff.

and doubtless more prolonged. The downward limit of change was controlled in part by exhaustion of the magnesium content of the waters and in part by the presence of locally developed impervious shale beds which protected the underlying limestone. The influence of thin shale seams in checking the descent of dolomitization at Specht;'s Ferry and at Clayton has been referred to. At these localities the alteration was halted before it reached the base of the Galena. At Dubuque, on the other hand, it extended down as far as the Decorah shale, and the whole of the Galena is dolomitic. Indeed, there is reason for believing that the alteration would have extended down still farther here and affected the Platteville if it were not for the presence of the shale bed. Such, in fact, is the state of affairs at Darlington, Wisconsin, thirty-five miles slightly north of east of Dubuque. At this place the Decorah shale member of the Dubuque region is absent, and we have a continuous section of dolomite from the base of the Platteville to the top of the Galena. There can be no doubt that the dolomitization of the Platteville was accomplished in this region at the same time as the dolomitization of the Galena and that the absence of the shale member at the top of the formation allowed the magnesian waters to descend farther here than in the Dubuque region.

The Saint Louis Limestone.—Irregular boundary relations are exhibited on a much smaller scale by the dolomitic and non-dolomitic portions of the Saint Louis limestone along the north bank of Indian creek two and one-half miles west of Farmington, Iowa (see figure 37). Here a bed of slightly disturbed, un-altered, gray, medium-grained limestone averaging about eight feet in thickness rests upon a bed of brecciated, yellowish, fine-grained, dolomitic limestone three to eight feet thick. The contact line is extremely irregular and fairly sharp. The marked difference in lithologic character of these beds and the irregular boundary between them suggests at once that they represent two distinct formations with disconformable relations, and in truth this was the interpretation first adopted by the writer. Further study, however, soon revealed the fact that these beds represent one continuous formation, and that the present rela-

24

tions resulted entirely from imperfect dolomitization of the limestone subsequent to its deposition. This interpretation is supported by the following facts: (1) If the beds are traced laterally a short distance it will be seen that the lower one has lost its dolomitic character and a perfectly continuous series of
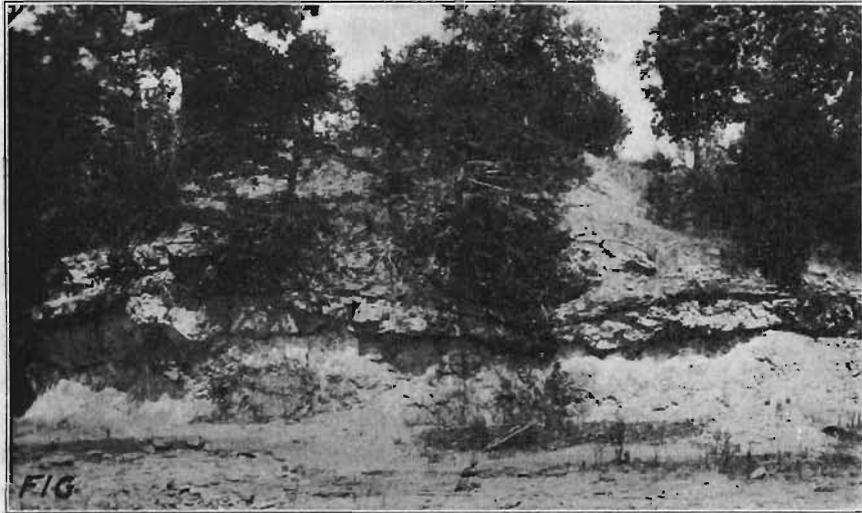

FIG. 37. Irregular boundary between limestone and dolomite beds of the Saint Louis formation. Section in north bank of Indian creek, two and one-half miles west of Farmington, Iowa.

gray limestone is found; (2) the boundary, although fairly sharp, is not a stratigraphic plane of separation; (3) evidences of imperfect dolomitization, in the form of bowlder-like masses and lentils of dolomite, are found in the limestones of the upper member.

That the alteration of the lower member took place subsequent to its brecciation is indicated by the fact that the brecciated structure now has been largely obliterated by welding, a process which normally accompanies dolomitization.

The Korallenoölith.—The dolomites of the Korallenoölith (Jura) also fail to be regularly marked off from the limestone, as was shown by Wichmann.[246] In the region about Selter and Ith the dolomite in this formation is not confined to a definite horizon, but encroaches upon the limestone both above and below within short distances.

[246]Zeitschr. Deutsch. geol. Gesell., Vol. 61, 1909, p. 392.

The French Jura.—Relations such as these have been shown by F. Pfaff[247] to exist in the French Jura. In the Wisent Valley between Streitberg and Muggendorf, the boundary of the dolomite in the upper portion of the formation with the limestone below descends and rises rapidly, but a short distance above Muggendorf the formation is dolomitic from top to bottom. This can be interpreted only as meaning that an original limestone formation was transformed to dolomite by a descending process of alteration.

Pseudo-Interstratification Effects.—The interbedding of limestone and dolomite has been postulated by some as evidence in favor of the primary origin of dolomite, but it is believed that most examples of so-called interbedding have resulted from differential dolomitization and that this feature furnishes much stronger evidence in favor of the alteration theories. The following facts lend support to this view:

1. The contact lines, though frequently sharp, are often wavy and do not coincide with the bedding planes.

2. The dolomite layers sometimes grade laterally into limestone and the limestone layers into dolomite.

3. The limestone layers are frequently mottled and streaked with dolomite.

4. The dolomite layers sometimes bear small irregular remnants of limestone.

EXAMPLES OF PSEUDO-INTERSTRATIFICATION.

In the course of this investigation many examples of pseudo-interstratification of limestone and dolomite have been encountered.

The "Calciferous" Limestone.—The "interbedded" series of limestones and dolomites exposed in the old Walton quarry opposite Harrisburg, Pennsylvania, appears to be best accounted for upon the basis of differential dolomitization, although Lesley[248] has concluded that the dolomite beds represent primary mechanical deposits. This is borne out by the relations of the dolomite to the limestone at a number of points here.

[247]Pogg. Annalen, 1851, p. 471.
[248]See ante p. 273.

Near the middle of the quarry face a bed of dolomite six feet
in thickness and dipping about 30° to the south appears in the
upper part of the opening. It is both overlain and underlain
fairly regularly by limestone, but in the lower part of the open-
ing its lower one-half passes abruptly into limestone and the bed
continues to the quarry floor as two distinct layers each three
feet in thickness (see figure 38). Samples of the dolomite and of
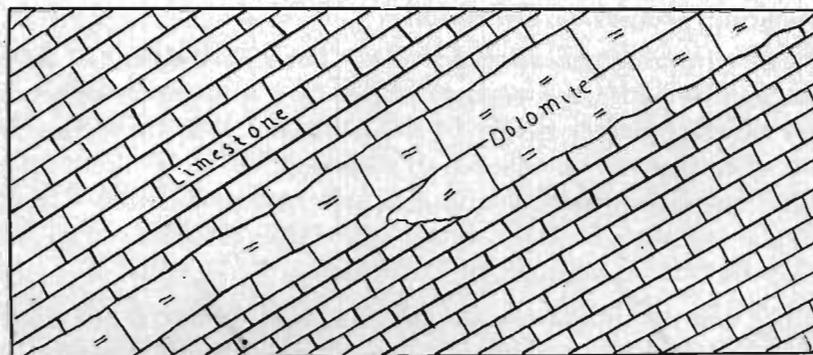
FIG. 38.   Showing lateral gradation of a dolomite layer into limestone. Walton Quarry,
opposite Harrisburg, Pennsylvania.

the limestone were taken at the same level and only a few inches
apart at the point where they grade into each other. These have
been analyzed by Dr. W. S. Smith with the following results:

	DOLOMITE	LIMESTONE
SiO$_2$	4.7	0.9
Al$_2$O$_3$+Fe$_2$O$_5$	1.1	0.3
CaCO$_3$	76.1	97.97
MgCO$_3$	18.1	0.83
	100.00	100.00

Further data upon the relationship of limestone and dolomite
are furnished by the following detailed section measured near
the north end of the quarry. The succession is from above down-
wards.

		FEET	INCHES
14.	Limestone, gray, fine-grained, with solution hollows	4	3
13.	Dolomite, grayish buff	2	6
12.	Limestone, dark gray, compact	1	
11.	Dolomite, light buff, seamed with crystalline calcite	1	8
10.	Limestone, dark gray when fresh but weathering lighter, compact	2	
9.	Limestone, gray, fine-grained, mottled with light buff patches of dolomite	3	
8.	Limestone, gray, fine-grained	1	6
7.	Limestone, gray, irregularly seamed with darker patches of dolomite		8
6.	Dolomite, dark gray, fine-grained	5	
5.	Limestone, gray, fine-grained, with seams of dolomite	2	
4.	Dolomite, dark gray, fine-grained	1	7
3.	Limestone, gray, fine-grained	1	
2.	Limestone, gray, fine-grained, mottled with patches of dolomite	3	
1.	Limestone, gray, fine-grained, upper six inches with irregular seams of dolomite	6	

Another instructive section is shown in a small pit near the middle of the quarry.

		FEET
5.	Limestone, gray, fine-grained	
4.	Limestone, gray, fine-grained, mottled with patches of dolomite	3
3.	Limestone, gray, fine-grained	2
2.	Limestone, gray, fine-grained, mottled with patches of dolomite	2
1.	Dolomite, the upper one-half grading laterally into fine-grained limestone mottled with dolomite. Exposed....	3

Near the south end of the quarry interesting relations again appear. At one point here a dolomite layer one and one-half feet thick bears irregular streaks and patches of unaltered limestone. Six feet higher up another layer shows similar relationships, while the limestone between is irregularly mottled with dolomite.

The Tribes Hill Limestone.—Relationships equally significant appear in the Tribes Hill limestone at Canajoharie, N. Y. The following section is exposed in the Allan quarry a short distance west of the village.

FEET INCHES.

UTICA:

10. Shale, dark, laminated 20

TRENTON:

9. Limestone, gray, subcrystalline, thinly bedded,
      with occasional shaly layers................ 19
    Disconformity.

TRIBES HILL:

8. Dolomite, bluish-gray, compact, heavily bedded
      below 11

7. Limestone, dark, compact, no dolomitic patches
      noted 2

6. Dolomite, bluish, compact, upper portion blotched
      with patches of lighter colored limestone.... 5   6

5. Limestone, gray, subcrystalline, conglomeratic,
      with dolomitic matrix   10

4. Dolomite, dark gray, compact, with seams and
      irregular patches of gray limestone in the
      lower part 3   8

3. Limestone, gray, subcrystalline, with some oölitic
      grains, bearing occasional thin seams and ir-
      regular patches of brownish dolomite........ 4   6

2. Dolomite, dark gray to bluish gray, compact,
      upper 8 to 10 inches mottled with irregular
      patches of limestone 2   8

1. Limestone, dark gray, dense, upper and lower
      portions slightly mottled with dolomitic
      patches. Exposed 4

The Chazy Limestone.—According to Hunt,[249] thin, irregular layers of ferruginous dolomite filled with crinoid stems consisting of pure $CaCO_3$ occur in the bluish, crystalline, fossiliferous Chazy limestones at Montreal. The matrix of the crinoid columns has the following composition:

PER CENT

Sand 9.01
$FeCO_3$... 27.03
$CaCO_3$ 40.95
$MgCO_3$ 24.19

A sample of the limestone taken one inch from the contact with the dolomitic layer yielded 18.4 per cent of insoluble matter and only .09 per cent of $MgCO_3$.

The Galena Limestone.—Leonard[250] has described a case of "interbedding" in the Galena limestone of Clayton county,

[249]Am. Jour. Sci., 2d ser., Vol. 28, 1859, p. 371.
[250]Ia. Geol. Survey, Vol. XVI, 1905, p. 249.

Iowa, and this has been examined by the writer. The exposure in which this relationship is shown appears in the southwest quarter of section 9, Volga township. The succession here from above downwards is as given below.

FEET

3. Dolomite, buff, massive 4
2. Limestone, gray, thin-bedded, with occasional small ir-
   regular patches of buff dolomite 8
1. Dolomite, gray to buff, heavily bedded................ 6-7

The contact of the limestone with the dolomite above and below is fairly regular and sharp, but the line of contact is not a stratigraphic plane of separation.

The Niagaran Limestone.—Pseudo-interbedding of limestone and dolomite is exhibited by the Niagaran limestone about two miles southeast of West Union, Iowa, at the "Devil's Backbone." The succession here from above downwards is as follows:

FEET

3. Dolomite, gray to buff, massive, vesicular............ 25-30
2. Limestone, gray, fine-grained, grading up into the bed
   above through 3 to 4 feet of mottled transition beds 20
1. Dolomite, buff, massive. Exposed..................... 12

The contact between beds 1 and 2 is not sharp, but the degree of dolomitization gradually decreases upwards through an interval of several inches. Similarly, the change from the limestone of bed 2 into the dolomite of bed 3 is not abrupt, but three to four feet of limestone in the upper part of bed 2 is blotched with small irregular patches and disseminated crystals of dolomite.

In the Williams and Davis quarry, located a few rods east of the "Devil's Backbone," beds 2 and 3 of the above section are again exposed. The contact of the beds at this point is abrupt and regular, and no well developed transition zone was noted. According to barometric measurements, the contact comes at the same level here as in the preceding section.

The Cedar Valley Limestone.—Instructive data on the relations of dolomite to limestone are furnished in an outcrop of Cedar Valley limestone at Portland, Iowa. The following section appears near the bridge over Lime creek, at this place:[251]

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[251]After Calvin, Ia. Geol. Survey, Vol. VII, 1896, p. 151.

FEET

6. Dolomitized bed with casts of thin laminar expansions
   of stromatoporoids, exposed between bridge and mill   5
5. Coarse granular dolomite in thin layers..............   3
4. White limestone with some stromatopores, the definitely
   bedded portion of the stromatopora reef...........   2
3. Stromatopora reef, with spheroidal corolla, but more
   perfectly stratified than at most exposures.........   4
2. White limestone, evenly bedded.....................   3
1. Dolomitized limestone in heavy layers..............   13

The contacts of beds 1 and 2, and of 4 and 5, are very abrupt, no transition of any sort being noted, but small irregular patches and seams of brownish, granular dolomite appear locally in beds 2, 3, and 4. In bed 4 an irregular network of thin dolomite streaks which tend to weather out in relief is developed. At the mill, a few rods above the bridge, bed 6 passes laterally from a uniformly dolomitized limestone through transition beds consisting of grayish, fine-grained limestone with streaks and patches of dolomite, to a nearly pure limestone, and all this within an interval of about four feet.

It is clear, then, that we are dealing here with pseudo-interbedding produced by the selective dolomitization of certain layers after the whole series was deposited.

A bluff section of Cedar Valley limestone and dolomite at Parker's Mill on Willow creek at Mason City, Iowa, also is of considerable interest in this connection. Calvin's description of this section is as follows.[252]

FEET

6. Stromatopora reef, equivalent of No. 5 of the Kuppinger
   quarry   4
5. White limestone somewhat split up by weathering....   14
4. Evenly bedded dolomite, in ledges varying from 3 to 30
   inches in thickness   12
3. Impure dolomite, breaking irregularly by exposure to
   weather, and containing many cavities lined by crys-
   tals of calcite 2½
2. Crumbling, calcareous, granular bed, light gray in col-
   or, with many modular and branching stromatopores,
   some Favosites and beautiful corolla of *Pachyphyl-
   lum woodmani*   1
1. Argillaceous limestone, dark drab in color, homoge-
   neous, but breaks up on exposure to frost...........   2

[252]Ia. Geol. Survey, Vol. VII, 1896, p. 149.

The contact of beds 2 and 3 is fairly regular and no boundary phenomena of importance were noted along it. But the boundary between beds 4 and 5 exhibits some interesting features. Thus numerous thin, discontinuous seams of fine-grained compact gray limestone are preserved in the upper portion of bed 4, and at some points the upper layer of this member is seen to pass laterally into unaltered limestone. Also, a transition from the dolomite of this member to the limestone above takes place locally through a thin zone of compact gray limestone with rather large crystals of dolomite disseminated through it. The upper boundary of this dolomite bed, therefore, is very indefinite, and is not an ordinary stratigraphic plane of separation.

"Interbedded" relations of limestone and dolomite are well developed in this formation at several localities in Mitchell county, Iowa. The discontinuous character of some of the dolomites in this region is well illustrated by a small exposure along the roadside two and one-half miles south of St. Ansgar. At the north end of the exposure a bed of unaltered gray limestone two feet eight inches thick, filled with colonies of stromatopores, is underlain by one foot of dense, white lithographic limestone. But as these layers extend southward a few yards they both pass abruptly into brownish dolomite at a point where they are intersected by a joint. In this dolomite the stromatopores are largely obliterated and the dolomitized lithographic stone is much coarser-grained than is the unaltered facies. The lower layer continues as dolomite as far as it may be traced in the exposure, but the upper layer which bears the stromatopores changes back within a few feet into imperfectly altered limestone which bears only thin seams and patches of dolomite.

The Chandler cliff section of the Cedar Valley limestone in the east bluff of the Cedar river one and one-half miles due west of Osage, Iowa, again furnishes some valuable data on the nature of the "interbedded" dolomites of this formation. The section here, modified after Calvin[253] in order to show the relations of dolomite to limestone in a more detailed manner, is given below.

[253]Ia. Geol. Survey, Vol. XIII, 1902, p. 313.

		FEET	INCHES
26.	Residual clay with thin weathered flakes of limestone	4	
25.	Dolomite, coarse-grained, weathered		6
24.	Limestone, lithographic, bearing imperfectly preserved stromatopores	1	
23.	Limestone, shaly	1	
22.	Limestone, light gray, lithographic	2	
21.	Shaly parting		1
20.	Limestone, lithographic, light gray, lower portion sometimes imperfectly dolomitized	2	6
19.	Shaly parting		2
18.	Limestone, light gray, lithographic, locally grading into dolomite in part	1	
17.	Dolomite, coarse-grained	1	
16.	Limestone, fine-grained, laminated	1	
15.	Dolomite, coarse-grained, brownish, in layers six inches to a foot in thickness, with casts of brachiopods in upper portion	4	
14.	Shaly parting		6
13.	Limestone, consisting of lithographic nodules in a granular matrix	1	2
12.	Limestone, light gray, lithographic, in one heavy layer, locally passing wholly or in part into coarser-grained, darker dolomite. In some parts only the upper and lower portions of the layer are altered. Again, in others the middle portion only is dolomitic. Where the layer is only slightly altered it bears small disseminated rhombs of dolomite which stand out in relief on weathered surfaces	1	2
11.	Shaly parting		6
10.	Dolomite, rather coarse-grained, dark gray, locally grading into compact gray limestone	1	6
9.	Shaly parting		2
8.	Limestone, lithographic above but granular below, in one heavy layer	1	6
7.	Limestone, light gray, lithographic	1	1
6.	Shaly decayed limestone	1	
5.	Limestone, light gray, crystalline	1	2
4.	Dolomite, yellowish, with occasional small remnants of limestone in basal portion; no fossils noted	9	
3.	Dolomite, yellowish, structureless, bearing casts of *Athyris vittata*, with a few remnants of dense gray unaltered limestone in which the shells of this fossil are preserved	12	
2.	Dolomite, in the form of two heavy, irregular beds which contain many shapeless cavities lined with calcite	5	
1.	Dolomite, in regular layers	15	

Pseudo-interbedding effects are typically shown also by the Cedar Valley limestones in the exposures at and near Fairport, Iowa. A section exposed in the north bank of the Mississippi river near the pottery works at this place is as follows:[254]

		FEET	INCHES
8.	Dolomite, rather hard, massive......	3	
7.	Limestone, fine-grained, hard, emitting a bituminous odor when struck with the hammer, imperfectly dolomitized locally	2	3
6.	Limestone, compact, charged with ramifying growths of Idiostroma, in some parts partly changed to dolomite.......................	1	6
5.	Carbonaceous material in the form of a thin seam		1
4.	Limestone, bearing large stromatopores, Amplexus and other fossils, imperfectly dolomitized locally	1	
3.	Dolomite, dark, with unaltered corolla of Cyathophyllum and with occasional stromatopores, locally passing wholly or in part into unaltered gray' limestone	1	6
2.	Dolomite, dark, filled with the nearly obliterated corolla of stromatopores and corals........		8
1.	Dolomite, soft, bluish, in rather heavy ledges, containing casts of brachiopods............	2	

Exactly the same relations are shown where this formation is exposed on Robinson creek, one-half mile west of Montpelier, Iowa. Here one bed of dolomite seven feet thick appears in the upper portion of the outcrop and another with an exposed thickness of five feet in the basal portion; and between these intervenes about four feet of limestone blotched with irregular patches of dolomite.

The Spergen Limestone.—The Spergen limestone frequently exhibits imperfect dolomitization phenomena and among these pseudo-interbedding is sometimes characteristically developed. Such relations are well shown in the old Fox quarry openings along the Chicago, Rock Island and Pacific railway track about one mile south of Belfast, Iowa. Near the mouth of a small ravine here the following section appears:

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[254]Revised after J. A. Udden, Ia. Geol. Survey, Vol. IX, 1898, p. 283.

FEET   INCHES

SAINT LOUIS:

7. Limestone, conglomeratic, imperfectly dolomi-
tized, consisting of dolomitic and non-
dolomitic blocks indiscriminately mingled,
marly towards the base................... 11
Disconformity.

SPERGEN:

6. Limestone, gray, crinoidal, thin-bedded........ 4
5. Dolomite, brownish, slightly arenaceous........ 4   4
4. Shale, calcareous and arenaceous............. 2
3. Dolomite, bluish, arenaceous 1–2
2. Limestone, gray, crinoidal, with a thin irregular
seam of buff dolomite in middle portion..... 4
1. Dolomite, brownish, arenaceous, in one massive
ledge. Exposed 10

Bed 2 has very wavy upper and lower boundaries due to the encroachment of the dolomite of the beds above and below upon it and at one point it passes entirely into dolomite for a short distance. In another exposure along the railway sixty rods farther south, the selfsame beds of the Spergen are dolomitic from top to bottom. The coarse-grained crinoidal limestone members of the preceding section are represented here entirely by fine-grained, brownish dolomite.

The Saint Louis Limestone.—Several occurrences of pseudo-interbedding have been noted in the Saint Louis limestone. In southeastern Iowa this feature is exhibited along with other phenomena of imperfect dolomitization. The formation is dolomitic from top to bottom at one locality while at another only a few miles away only a few layers are dolomitic. For example, in a bluff on Mud creek one mile east of Lowell, the Lower Saint Louis is represented by a massive buff dolomite thirty to forty feet in thickness, while in another section three miles northwest of Denmark and only about five miles away the selfsame formation is represented entirely, with the exception of a single dolomitic layer about three feet thick, by fine-grained, compact, gray limestone.

In the government quarries at Little Rock, Missouri, the Saint Louis shows similar relations on a smaller scale. At the south end of the northernmost opening there appears a bed of

buff dolomitic limestone five feet in thickness, lying between beds of unaltered, compact, fine-grained limestone. Northward in the quarry face, however, the upper and lower portions of the dolomite grade gradually into limestone. At 100 yards its thickness has decreased to 3½ feet and at 150 yards the dolomite has so nearly disappeared that only thin seams and stringers remain. A few yards farther north no trace of dolomite is to be seen, but the bed has changed completely into a medium-grained, slightly oölitic limestone.

Another remarkably good exhibition of "interbedding" of limestone and dolomite doubtless due to differential dolomitization is found in the Saint Louis limestone in the vicinity of St. Louis. The following table, comprising a description of each individual bed and its composition, compiled from the report of G. E. Ladd,[255] will show the relations existing in the Martin Lorenz quarry, which is situated along the Iron Mountain and Southern railway track near Cahokia Street. The high siliceous content of some of the dolomitic layers of this section is worthy of notice.

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[255]Mo. Geol. Survey, Bull. 3, 1890, pp. 54, 55, and 76.

TABLE VII.

DESCRIPTION

Limestone, light gray, darker towards top, fine-grained......................
Limestone, as above ....
Limestone, light yellow and gray, soft ....
Limestone, light and dark gray, varying texture, compact, brittle, hard........
Limestone, gray, fine-grained, jointed ....
Limestone, light gray, fine-grained, color and texture variable.................
Limestone, dull gray to yellowish, harder towards base.........................
Limestone, brownish and gray, coarse-grained, shaly near top.................
Limestone, as in bed above ....
Limestone, dull gray, very fine-grained ....
Limestone, drab, hard, brittle, lithographic, shale seam 1 in. thick at base....
Limestone, gray, hard ....
Limestone, light drab, with dark bands ....
Limestone, dark gray, carries layer of chert...................................
Limestone, light drab, fine-grained, layer of chert 3 feet from base............
Limestone, dark gray, bearing geodes lined with calcite crystals...............
Limestone, light gray, soft, chert concretions near top.......................
Limestone, gray, coarse-grained ....
Limestone, as above ....
Limestone, dark gray to brownish, lower sixteen inches cherty..............
Limestone, brown, otherwise like bed above...................................
Limestone, drab, hard, brittle, fine-grained, lithographic.....................
Limestone, dark gray, coarse-grained, hard, in three ledges...................

Total Thickness ....

The Upper Jurassic Limestone.—Nahnsen[256] has mentioned a case of pseudo-interbedding in the Upper Jurassic of North Germany. Here a horizontal seam of dolomite with wavy boundaries appears in a limestone member which rests on a bed of dolomite. Near its borders the seam shows a pseudo-brecciated effect due to the presence of irregular remnants of limestone in the dolomite.

III.   Evidence Bearing on the Leaching Theories.

THE SURFACE LEACHING THEORY.

Of the points which may be advanced in support of the surface leaching theory, the following are perhaps the most important:

1.   The development of dolomite along lines of weakness, such as fractures, in limestone.

[256]Neues Jahrb., Beil. Bd. 35, 1913, p. 277.

THICKNESS		COMPOSITION			
FT.	IN.	Insoluble	Al$_2$O$_3$+Fe$_2$O$_3$	CaCO$_3$	MgCO$_3$
1	6	6.53	0.83	83.85	8.16
1	10	8.02	1.01	79.40	10.81
0	8	9.97	1.07	70.80	10.86
2	10	3.44	.37	92.05	3.67
2	6	4.61	.34	93.85	.99
2 ·	6	6.08	.61	78.15	15.81
4	2	11.63	3.10	52.85	29.25
3	0	2.83	.19	94.75	.97
2	4	6.79	.55	90.55	1.06
0	5	8.77	1.35	56.45	31.95
1	0	7.64	.80	84.75	5.27
0	9	11.02	2.50	57.80	26.33
1	10	6.29	.95	84.95	5.98
3	11	1.97	.35	87.60	8.66
8	2	10.40	11.75	68.30	17.22
0	8	3.20	.40	93.20	1.44
2	0	19.96	4.80	51.60	19.22
1	10	2.32	.26	94.35	1.70
0	10	1.64	.25	95.70	1.10
4	0	5.77	.43	89.95	2.23
3	9	2.84	.25	93.60	2.23
1	6	2.72	.35	93.75	2.38
3	4	2.77	.40	92.40	3.22
56	4				

2. The apparent tendency of dolomite to be developed in limestone at those points where CO$_2$ and humus acids are most abundant.

3. The vesicular character of some dolomites.

4. The existence of stalactite and stalagmite deposits of nearly pure CaCO$_3$ in caverns in dolomitic limestone.

5. The increase in the magnesium content of weakly dolomitic limestone as an accompaniment of weathering.

The Development of Dolomite along Fractures.—The occurrence of dolomite along fractures in limestone has been taken by some to mean that dolomite so related has been formed by the leaching out of the excess of lime from a weakly dolomitic limestone by solutions which circulated along these lines of weakness. This would seem to apply especially well to certain

dolomites of the Lahn district, as pointed out by Grandjean. Bischof,[257] in summarizing the data furnished by this district, says:

Wherever the fissures and cracks of the slightly inclined limestone strata have facilitated the penetration of water, there the production of dolomite appears to have taken place to the greatest extent. The strata which, by their exposed situation, were most subject to this penetration, present the most advanced state of alteration. But in the lower beds of limestone there has been but little, if any, production of dolomite. The dolomite, and the partially altered beds of limestone adjoining it, are traversed by numerous cracks, fissures, and cavities; and where the alteration is more advanced, the iron and manganese compounds, to which the colour is due, have been separated . . .
Since the alteration of limestone, in consequence of the production of dolomite, may often be traced, even in a hand specimen, from the first stage, to the total conversion into an argillaceous mass, Grandjean infers that where the level character of the surface facilitates the continuous action of water, the limestone may be ultimately converted into clay.

An analysis by Bischof of a sample of limestone from Tiefenbach in this district showed it to have the following composition:

	PER CENT
$CaCO_3$	69.90
$MgCO_3$	2.34
$FeCO_3 + MnCO_3$	8.18
Clay	20.43

As to the relative importance of leaching as compared to ground water dolomitization in the production of the Lahn dolomites, there may be some difference of opinion. If the analysis given above is representative of the limestones of the district, it is difficult to understand how leaching alone could give rise to the dolomite, since the proportion of clay and of iron and manganese in the rock would tend to increase so much more rapidly than the magnesia that the latter would be largely obscured. But that the magnesia liberated by the complete breaking down of the limestone into clay on the surface may have aided in the formation of dolomite along fractures in the lime-

[257]Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 193.

stone below must be regarded as possible, since deposits of residual clay bearing iron and manganese ores are common in the district.

Local Development of Dolomite where CO₂ and Humus Acids are Generated.—If it could be shown positively that local occurrences of dolomite in limestone are in some way related to the amount of CO_2 and humus acids permeating the rocks, more tangible evidence of the production of these dolomites by leaching would be available. Phillipi[258] has obtained some data bearing on this point, but the evidence cannot yet be regarded as conclusive. Thus, the Conchodon limestone, which is only locally and imperfectly dolomitized, seems to be most strongly altered where it is permeated by water rich in CO_2 and humus acids. In the heights, on the other hand, where waters poor in CO_2 penetrate the rock, it is either not at all, or but little altered. The area examined by Phillipi, however, was not sufficient to prove that these relations were constant and pending further study too much emphasis should not be placed upon this apparent relationship.

The Vesicular Character of Some Dolomites.—Dolomites formed by surface leaching should be expected to be very porous and vesicular as a result of the removal of large quantities of $CaCO_3$, but not all vesicular dolomites have resulted from leaching, since it is well known that shrinkage effects characterize many dolomites which have resulted from the replacement of limestone. This criterion, therefore, must be applied judiciously. When, however, a dolomite possesses a porosity exceeding 12 per cent, the balance of evidence is in favor of the theory that leaching operated to some extent at least.

Certain dolomites of the Carboniferous of Ireland exhibit considerable solution effects according to Hardman.[259] For instance, at Drumreagh near Coal Island beds of dolomite interstratified with ordinary blue fossiliferous limestone are very cavernous, as fully half of the rock has been removed and has left numerous spar-coated cavities. But dolomites exhibiting so-

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[258]Neues Jahrb., 1899, Vol. I, p. 44.
[259]Proc. Roy. Irish. Acad., 2d ser., Vol. 2 (Science), 1875-77, p. 723.

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lution effects are rare and unless we assume that the gradual settling and re-accommodation of the limestone has accompanied leaching it is difficult to conceive of dolomite having been formed extensively in this manner. Hall and Sardeson,[260] to be sure, have advocated that a great reduction in volume by means of leaching has accompanied the formation of the Lower Magnesian series of the Upper Mississippi Valley, but the field evidence of such a volume reduction is wanting. Some of the obstacles encountered by the leaching theory in this respect have been demonstrated by Skeats,[261] who showed that an original rock containing 1 per cent of $MgCO_3$ would have to be removed by solution to the extent of 80 per cent before the $MgCO_3$ of the remainder reached 5 per cent, and to the extent of 90 per cent before the $MgCO_3$ content attained the proportion of 10 per cent.

On the whole, therefore, the shrinkage phenomena of dolomites are not favorable to the idea of their having been formed extensively by surface leaching alone. But there can be no doubt that leaching has given rise to considerable enrichment of the magnesium content of limestones already dolomitic. For example, the unaltered calcareous skeletons of fossils have been leached out of most fossiliferous dolomites and when large numbers of these were present originally, their removal must have given rise to a notable increase in the proportion of the magnesium in the rock. The coral reef facies of the Niagaran dolomite of the Upper Mississippi Valley must have been considerably enriched in magnesia in this way.

Stalactite and Stalagmite Deposits in Dolomitic Limestones.—
The occurrence of stalactite and stalagmite deposits of nearly pure $CaCO_3$ in the caverns of dolomitic limestones has been cited as positive proof of the possible operation of leaching on a large scale. Several such occurrences are known. Hardman,[262] upon analyzing both a stalagmite and a sample of the dolomitic limestone from the Dunmore Cave of Kilkenny county, Ireland, found a marked contrast in the magnesia content of the two specimens. The analyses are reproduced below.

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[260] Bull. Geol. Soc. America, Vol. 6, 1895, p. 167.
[261] Quart. Jour. Geol. Soc. London, Vol. 61, 1905, p. 132.
[262] Proc. Roy. Irish Acad., 2d ser., Vol. 2 (Science), 1875-77, p. 718.

	LIMESTONE PER CENT	STALAGMITE PER CENT
SiO_2	1.92	....
$Fe_2O_3 + Al_2O_3$	4.32	.23
$CaCO_3$	68.21	97.12
$MgCO_3$	24.00	.79
$FeCO_3$	.90	1.86
Total	99.35	100.00

Similarly, Högbom,[263] upon analyzing the stalactite from caves in the Bermuda reef stone, found only .18 and .68 per cent of $MgCO_3$ respectively, while the reef stone itself contains about five times this amount.

The presence of veins and druses of calcite in dolomitic limestone also must be taken as indicating that some removal of $CaCO_3$ from these limestones has taken place. Veinlets of calcite commonly traverse the deformed Cambro-Ordovician dolomitic limestones of the Appalachian region.

The operation of surface leaching, on a small scale at least, then, must be regarded as certain. But there is little evidence that enrichment of limestones in magnesium in this manner has gone far.

Increase in Magnesium Content with Weathering.—The progressive increase in the magnesia content of limestones low in $MgCO_3$ with weathering must be regarded as lending strong support to the surface leaching theory. Hiltermann[264] found such a rise in the proportion of $MgCO_3$ in the weathered limestones of the German Trias. Thus, a fresh sample of the Grenz limestone contained 54.69 per cent of $CaCO_3$ and 3.69 of $MgCO_3$, while the weathered rock yielded 11.96 of the former and 5.83 of the latter. Although considerable importance has been attached to these results by some, it is difficult to understand how this process could operate to produce other than very impure, argillaceous dolomites, because of the marked increase in the proportion of the insoluble matter of the rock as an accompaniment of the leaching. Unless it be assumed, therefore, that the original limestone is almost ideally pure, a type of limestone which is rare in nature, the leaching theory meets with grave difficulties.

[263] Neues Jahrb., 1894, Vol. 1, 271.
[264] Quoted by Phillipi, Neues Jahrb., 1899, Vol. I, p. 34.

THE MARINE LEACHING THEORY.

That sea water has the power to remove the $CaCO_3$ more rapidly than the $MgCO_3$ from limestone and calcareous ooze low in the latter constituent must be admitted by all. Some of the facts which indicate this are:

1. The testimony of recent and near-recent marine calcareous deposits.

2. Actual demonstration of marine leaching on a small scale.

3. Obliteration effects and porous structures in recent dolomitic coral reefs.

Testimony of Recent and Near-Recent Marine Calcareous Deposits. — Högbom[265] has sought to show that certain marine Quaternary marls of Sweden exhibit a progressive increase in the $MgCO_3$: $CaCO_3$ ratio the further they lie from their original source, a Silurian argillaceous rock. (See Table VI, p. 293.) Thus, a sample nearest the source yielded 32 parts of $CaCO_3$ and 1.2 of $MgCO_3$, while the sample farthest away gave only 3.3 parts of $CaCO_3$ and 1.2 of $MgCO_3$. This is interpreted by him as meaning that the longer the sediment was in suspension and the farther it was carried from the source the more the $CaCO_3$ was removed and the proportion of $MgCO_3$ increased. The analyses of deep sea deposits furnished by the Challenger Report also are regarded by Högbom as significant in this connection (see Table V, p. 293), but the $MgCO_3$ content of these is low, as in the case of the above mentioned marls, since it does not exceed 2.1 per cent, while the $CaCO_3$ content also is low for the most part, and the insoluble matter is very high. It is difficult to understand, therefore, how these data can be applied in predicting the conditions of the formation of extensive dolomites nearly free from insoluble matter yet rich in $MgCO_3$.

Actual Demonstration of Marine Leaching.—That marine leaching is capable of enriching the magnesia content of calcareous deposits, on a small scale at least, has been proven both by Murray and Irvine and by Högbom. For instance, Murray

[265]See ante, p. 293.

and Irvine[266] found a much higher per cent of $MgCO_3$ in the outer portions of the umboes of the giant clam, *Tridacna gigas,* than in the internal and more newly formed shell layers, and Högbom[267] has demonstrated the operation of leaching in the Bermuda coral reefs. Thus analyses by A. R. Manzelius of the reefstone and of the fine lagoon mud derived from it showed a greater proportion of $MgCO_3$ in the latter than in the former.

	$CaCO_3$	$MgCO_3$
Coarse reefstone	95.43	1.64
Reefstone with gastropod fragments......	96.11	2.13
Coarse white lagoon mud.................	97.47	1.79
Fine terra-cotta colored lagoon mud.......	92.93	4.04

Upon the strength of these data the conclusion is reached by Högbom that if the fine mud were suspended long enough its enrichment in magnesia might proceed to such an extent that a dolomitic sediment might in the end result, but definite proof of this is wanting.

Obliteration Effects and Porous Structures in Recent Dolomitic Coral Reefs.—Shrinkage and obliteration effects are not necessary accompaniments of marine leaching, since the removal of $CaCO_3$ may sometimes go on in the fine calcareous sediment as it is being deposited, as in the lagoons of the Bermuda reefs. Where, however, the leaching is supposed to have taken place in coral reefs, a porous structure should be shown by these. The more dolomitic portions of the Funafuti reef are said to be cavernous and Judd[268] states that much of the mineral substance of the skeletons of calcareous algæ appears to have been removed. But Skeats[269] points out that the dolomites of the upraised coral islands of the southern Pacific, which exhibit all stages of replacement by dolomite, also are cavernous. Shrinkage and related phenomena of dolomites cannot, therefore, be regarded as indicative of their having been formed by marine leaching.

[266]Cited by Judd, The Atoll of Funafuti, p. 378.
[267]Neues Jahrb., 1894, Vol. 1, p. 279.
[268]The Atoll of Funafuti, p. 384.
[269]Bull. Mus. Comp. Zool., Vol. 42, 1903, p. 115.

PETROGRAPHIC EVIDENCE.

In many instances dolomite can be distinguished from calcite in thin section by its tendency to take on a characteristic yellowish tint and by its more perfect rhombohedrons, which are almost invariably larger than the associated calcite grains and are much clearer. For careful differentiation of the two carbonates, however, microchemical tests must be resorted to. In the present investigation Lemberg's solution[270] yielded very satisfactory results. Upon applying this solution to the section the calcite is colored pink, while the dolomite remains unaffected, and in this way the most intimate relations of the two minerals are made clear. It should be stated, however, that this test furnishes no reliable guide to the exact amount of magnesia in the rock, for homogeneous crystals containing not more than 23 per cent of $MgCO_3$ react in the same way as normal dolomite. But this in truth must be regarded as a distinct advantage, for alterations of only a slight degree are indicated as well as the more marked ones.

I. Evidence Bearing on the Primary Deposition Theories.

A. *The Chemical Theory.*—Some compact dolomites possess an extremely fine and uniform grain, and this feature has led some to believe that such dolomites represent chemical deposits. For instance, Daly[271] has described a pre-Cambrian dolomite of the Rocky Mountains region which consists of roughly rhombohedral and anhedral grains, the former of which range from .01 to .03 millimeter and the latter .005 to .03 millimeter in diameter. By him the fine and monotonous grain of this rock is regarded as strong evidence of its primary character. In order to test the validity of this argument the finest grained dolomites of unknown origin encountered by the writer in these studies were compared with the finest grained dolomite of known secondary origin. Thus the Jefferson City dolomite of the Ozark region, whose origin is not known from the field evidence, contains unusually dense and compact layers which are seen

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[270]For the composition of this solution and method of preparing it see W. F. Hillebrand, Bull. U. S. Geol. Survey No. 422, 1910, p. 211.
[271]Bull. Geol. Soc. America, Vol. 20, 1909, p. 153.

under the microscope to be made up of minute granules ranging from .001 to .045 millimeter in diameter, although the majority of the grains are below .003. The size of grain of this rock then, according to Daly's argument, suggests that it is a chemical precipitate. But the strength of this interpretation is greatly weakened by the fact that an equally fine-grained dolomite, which is known from the field evidence to be an alteration product, has been found in the Fayette limestone near Bertram, Iowa. The latter dolomite has resulted from the dolomitization of a dense, lithographic-like limestone with the approximate retention of the original texture.

B. *The Clastic Theory.*—As regards the possibility that some dolomites are of clastic origin, none has been found which exhibits any signs of clastic structure. But that the original structure in rocks of this type might have been obliterated during recrystallization is easily conceivable. Some of the dolomites of supposed clastic origin do, however, show other features which suggest a primary origin. For example, fragments of calcareous fossils showing no trace of corrosion are common in the impure siliceous dolomites of the Keokuk formation at Keokuk, Iowa. The experience of the writer has been that such fossils as occur in secondary dolomites are at least partly obliterated by the invasion of dolomite. The fact that certain impure, siliceous dolomitic limestones are seen in thin section to be clouded with dark inclusions also might be regarded as possible evidence of their clastic origin, since no known secondary dolomites have been observed to exhibit this to the same degree.

II. Evidence Bearing on the Alteration Theories.

Turning now to the petrographic evidence bearing on the alteration theories, we have much more definite data. Indeed, by virtue of the fact that the transformation in many instances has been halted before it proceeded to completion, we are often able to trace all stages of dolomitization from a limestone showing only incipient alteration to a good dolomite. Thus, it is possible to describe the steps normally passed through during the transformation of a limestone to dolomite.

The Alteration of Fine-Grained Limestones.—So far as the testimony of the microscope goes, the fine-grained limestones are more susceptible to alteration than the coarse-grained ones, a fact which is in keeping with the laws of chemistry. The evidence also points to the fact that the alteration does not proceed in exactly the same manner in the two types of limestone.

The alteration of fine-grained, compact limestone appears to be accompanied normally by a notable increase in size of grain. Frequently the average diameter of the dolomite crystals formed is many times greater than that of the original calcite grains. But in rare cases, such as that of the dense dolomite of the Fayette formation referred to above, the original structure and texture are approximately retained. In the dolomitization of such fine-grained limestones the replacement in some cases proceeds uniformly over a large front, but in most instances it begins at many centers throughout the rock and spreads outwards from these; or if the rock possesses fine stratification the replacement may follow closely these original lines of weakness in the early stages. In those cases where the alteration began at certain favorable centers and spread out from these, fucoid markings in a few instances have served as the nuclei, as in case of the Tribes Hill limestone. The exact nature of these fucoids is not revealed in thin section. When they have been changed to dolomite their original structure is of course mainly lost, but where they are still partly or wholly preserved in the unaltered condition they are differentiated from the adjacent limestone only by the fact that the calcite grains are clouded with dark inclusions suggesting carbonaceous material. None of them has been found to possess any signs of organic structure.

Again, there are cases in which the dolomitization in its early stages is known to have attacked calcareous algæ. This is particularly true in the Chazy limestone of the Lake Champlain region, where it exhibits evidences of incipient alteration. There are several specimens from this region in the writer's collection which show algæ of the Girvanella type in an advanced stage of alteration while the adjacent limestone areas are but little if at all affected. Still other fossils are known to have been selectively

replaced in the early stages of dolomitization. Thus, dolomitized tests of the gastropod Ophileta have been observed in unaltered Beekmantown limestones at Ft. Ticonderoga, New York, and the tests of Maclurea are similarly affected in the Chazy near Shoreham, Vermont. Similarly the tissues of Stromatopores have been selectively replaced during the imperfect dolomitization of the Cedar Valley limestone at Fairport, Iowa. There can be no doubt that fossils frequently have served as the starting point in the early stages of dolomitization. But there is convincing evidence that this has not always been the case, for many instances are known where the alteration has proceeded independently of the organisms imbedded in the rock. In the Galena limestone of northeastern Iowa and in the Elvins formation of southeastern Missouri the transformation is inaugurated by the appearance of minute patches or isolated crystals in the fine-grained limestone and the gradual enlargement of these areas at the expense of the limestone. But whatever the nature of the early stages of dolomitization, whether they were influenced by organisms or not, the later stages are always the same, and uniformly dolomitized limestone is the ultimate product in each case.

As the dolomitization spreads from the original centers the limestone typically is not completely replaced, and although the dolomitic patches may appear to be made up entirely of dolomite crystals, they may not bear more than 23 per cent of $MgCO_3$, nor is the limestone in all cases uniformly replaced. Small irregular remnants and streaks of limestone are passed over and become incorporated in the dolomite area. The boundary between the limestone and the spreading dolomite may or may not be abrupt. In a few examples in which it is abrupt, veinlets of dolomite shoot out into the limestone in advance of the main dolomite areas, and on the whole the tendency is to produce a "pseudo-brecciated" effect. So far as the experience of the writer goes, these abrupt contacts are most characteristically developed in the early stages of the alteration of limestones which have undergone recrystallization prior to dolomitization. To illustrate, the Saint Louis limestone, which exhibits this phenomenon at several localities in southeastern Iowa, is

known to have experienced mashing and brecciation previous to the time it was altered, a fact which indicates unquestionably that it had already recrystallized.

Where the boundary is gradational, on the other hand, as is usually the case, rhombohedrons of dolomite, variable in size but usually nearly perfect in their development, are disseminated through the limestone a short distance in advance of the dolomite area. The regular rhombohedral outline of these disseminated crystals is in strong contrast to that of the crystals of the dolomite area, which have interfered with one another in their development, thus giving rise to an interlocking structure. The usual large size of the isolated dolomite crystals as compared to that of the associated calcite grains also is a striking feature. This is especially true in the case of a Devonian lithographic limestone near Osage, Iowa, which shows incipient dolomitization. The calcite grains of the rock do not exceed .003 millimeter in average diameter, yet the dolomite metacrysts attain a maximum diameter of .75 millimeter. A similar relationship is exhibited, but to a lesser degree, by the Joachim limestone of southeastern Missouri. A sample of the limestone streaked with dolomite shows a range in diameter of the calcite grains from .001 to .015 millimeter, while the associated dolomite crystals range from .005 to .145 millimeter in diameter. Many other examples exhibiting a similar relationship could be cited. The great increase in size of grain which normally results from the dolomitization of fine-grained limestone is in this way accounted for. It should be stated, however, that many of the above mentioned metacrysts of the Devonian lithographic stone are not perfectly developed. Many of them are filled with minute unoriented inclusions, which evidently represent small calcite grains enveloped in the crystals as they grew. Furthermore, some of the dolomite metacrysts show evidences of zonal growth where they are in contact with the unaltered limestone, and a single thin band of calcite appears within their borders. It is a singular fact that these inclusions and zonal growths are never seen in the more completely dolomitized areas, a fact which suggests that in these the calcite grains and bands, if they once existed, have been changed over to dolomite.

The Alteration of Coarse-grained Limestones.—In considering next the alteration of the coarse-grained limestones, we meet with somewhat different phenomena, although the ultimate effect is the same. In these mottling does not seem to be the rule, and the effect on the size of grain is quite the reverse of that exhibited by the fine-grained limestones. In these the dolomitization is accompanied by a decrease in size of grain which becomes the more marked as the original calcite grains are larger. Here, then, we have a great equalizing process tending to produce coarser-grained rocks from fine-grained ones and finer-grained rocks from coarse-grained ones.

Typically the alteration of coarse-grained limestone proceeds by an attack on the matrix in the early stages, with the formation of small scattered dolomite rhombs, and then by invasion of the large calcite grains, whether they be fossil fragments or ordinary crystals, both by corrosion of their borders and by the breaking down of their interiors. In this process the large calcite grains are broken down into aggregates of smaller dolomite grains, and in the end the original structures and textures are obliterated.

This is the method of dolomitization of the coarse-grained crinoidal limestones of the Burlington and Keokuk formations of the Central Mississippi Valley. In the alteration of certain coarse-grained limestone layers of the Beekmantown at Plattsburg, New York, however, the above described order of replacement seems to have been reversed. This limestone is uniformly medium-grained to coarse-grained and is dotted with the tests of foraminifera and with other areas of a variety of shapes and of a dark tint which are doubtless also organic, although they are structureless and indeterminate. Strangely enough many of the interiors of the foraminifera and of the associated dark areas are either partly or wholly changed to dolomite, while the surrounding matrix is practically unaffected. Where the alteration is incomplete, numerous perfect isolated rhombs of dolomite are developed, but where it is more advanced the crystals interfere and are irregular in outline. By this method of dolomitization mottling on a microscopic scale is produced.

The coarse-grained Chazy limestones of Valcour Island exhibit mottling on a much larger scale, but organic factors seem to have played no part in the production of this phenomenon. The dolomite areas of this rock are fine-grained, although they have resulted from the alteration of coarse-grained limestone, as shown by the presence of corroded remnants of large calcite crystals and fossil fragments surrounded on all sides by minute crystals of dolomite. Some of the crystals preserved are more than 200 times as large as the dolomite grains about them.

The Alteration of Oölitic Limestones.—In the dolomitization of oölitic limestones the alteration of the oölite grains appears to proceed, in most cases at least, independently of the matrix and probably more often in advance of the alteration of the matrix than contemporaneously with it. Several examples of dolomitized oölites are known.

A sample of oölite from the Elbrook limestone in a quarry at West Waynesboro, Pennsylvania, has the appearance of a good oölite megascopically, but under the microscope the oölite grains are represented only by structureless, rounded, darker areas scattered here and there throughout the field. These are for the most part replaced by dolomite, while the matrix, except for a few small, irregular patches of this mineral, is unaltered. Precisely the same relations are exhibited by an oölite from the imperfectly dolomitized limestones of the Elvins formation near Elvins, Missouri; by the Lucas oölite as developed near Sylvania, Ohio; and by the Tribes Hill oölite at Canajoharie, New York.

In a dolomitic oölite from the Allentown limestone near South Bethlehem, Pennsylvania, somewhat different relations are shown. In thin section the characteristic radial and concentric structure of oölite is not exhibited, but the original outline of the grains is retained in every case. In a few examples the grains are completely altered to dolomite, but even there a faint, dark line marks their borders. But most of the grains are only partly altered, and still consist of an inner nucleus of cloudy dolomite with an outer rim of transparent calcite. The matrix is everywhere dolomitic except for occasional minute irregular areas of calcite. The unaltered calcite rims of the oölite grains have a

perfectly regular, rounded outer border which shows no corrosion effects even though they are completely surrounded by dolomite. Their inner borders, however, are much less regular, indicating that the nuclei of dolomite were formed by a process of dolomitization which began at the center of the grains and spread outwards. The alteration of the oölite grains then proceeded independently of the alteration of the matrix. The oölite which occurs at the basal portion of the Oneota dolomite at Mc-Gregor, Iowa, exhibits almost identically the same features as the Allentown oölite, but in this rock the original calcite remnants have been replaced by silica since dolomitization took place. Every step may be traced in the transformation of the oölites from wholly unchanged grains to completely altered ones.

Only one uniformly dolomitized oölite has been found in these studies. This is from the Hoyt limestone near Saratoga Springs, New York. It consists of rather large and distantly placed rounded to sub-ovate dolomitized oölite grains in a dolomite matrix. Quartz grains, of which the larger have rounded but the smaller very irregular outlines, are disseminated throughout the rock, appearing both in the oölite grains and in the matrix. The dolomite crystals within the areas of the original oölite grains do not extend beyond the borders of these and behave independently of those of the matrix under crossed nicols, a fact which indicates that even in this rock the dolomitization of the two areas proceeded separately.

CONCLUSIONS.

Considering all the evidence, there seems to be no escape from the conclusion that the great majority of the stratified dolomites have had their inception in the alteration of limestones. It will not be denied, however, that some dolomitic formations of minor importance have had a different origin. The possibility of direct chemical precipitation of dolomite from the sea, on a small scale at least, has not been wholly disproven, and there is evidence that some impure dolomitic limestones of minor importance may represent original clastic deposits. That such a method of dolomite building is possible is suggested by the resistant character of dolomite rocks and the tendency of the coarser-

grained varieties to weather to a dolomite sand. If such a dolomite sand should be carried to the sea and incorporated in a sedimentary series, an impure dolomitic rock might result.

As regards the possibility that organizms have ever given rise to more than very weakly magnesian limestones, this seems doubtful, as has been shown. But that limestones which are originally weakly magnesian may become enriched in magnesium more easily and more rapidly than those nearly free from this constituent is not only conceivable but very probable.

The importance of marine and surface leaching in the production of a dolomite is believed to have been overemphasized. There can be no doubt that this process has enriched in magnesium the more vesicular dolomitic limestones. But these must have been rich in this constituent before leaching began. The leaching theory, therefore, does not explain the ultimate source of the magnesium. It merely shows how the magnesia content of a rock originally magnesian can be enriched.

Time and Place of Dolomitization.—To return now to the dolomites which have resulted from the alteration of limestone: there are many reasons for believing that the more extensive of these have all been formed beneath the sea, and that dolomitization effected by ground water is only local and very imperfect. Some of the features which lend weight to this view are as follows: (1) The dolomite areas of mottled limestones are believed to have undergone recrystallization at the same time as the associated limestone areas, as suggested by the occasional development of zonal growths of calcite and dolomite. (2) In imperfectly altered limestones the dolomite is seen to follow original lines of weakness rather than secondary structures such as joints or fractures. (3) In most cases of mottling the dolomitization appears to have spread out in every direction and to have progressed uniformly, as we should expect it to in an unrecrystallized rock, rather than to have proceeded by forming veinlets and stringers in the early stages. (4) The existence of perfect rhombs of dolomite in many imperfectly altered limestones suggests that the latter had not yet solidified when dolomitization took place. (5) The widespread extent and nearly

uniform composition of many dolomites indicates that they must have been formed by an agent capable of operating uniformly over wide areas.   (6) An adequate source of magnesium for transforming extensive limestone formations into dolomite is found only in the sea, which contains many times as much of this constituent as ordinary ground water.   (7) Many dolomites are directly and regularly overlain by pure limestone formations or by thick shale beds, proving that they must have been formed before these overlying beds were deposited.

Some dolomites of minor importance, such as those associated with ore deposits, and probably most if not all of those related to fractures, must have been formed through the agency of ground water. But in general ground water is incapable of carrying dolomitization far. Study of analyses of ground water and of river water shows these to be uniformly low in magnesium, while this constituent normally is greatly exceeded in amount by lime.   How, then, could such waters dolomitize limestone when they already contain $CaCO_3$ far in excess of the $MgCO_3$? The law of mass action speaks strongly against ordinary waters being able to accomplish extensive dolomitization. In the case of mineral springs and the mineralizing solutions which are related to ore deposition, however, it is conceivable that magnesia might be present in sufficient proportions to accomplish local dolomitization, and doubtless most vein dolomites have been so formed.

With reference to the possibility of dolomite ever having been formed extensively through the action of pneumatolytic agencies on limestone: this also is improbable. Both Fournet[273] and Wissman[274] have pointed out that the dolomites of the Tyrol, which formerly were regarded by Von Buch and others as having been formed in this manner, are in no way related to the melaphyr which there penetrates the limestone. It must be regarded as possible, however, that small amounts of dolomite might be formed locally when limestone is permeated by volcanic gases bearing magnesia. But this has little bearing on the problem at hand.

[273]Bull. Soc. Geol. France, 2d ser., Vol. 6, 1849, p. 502.
[274]Cited by Bischof. Elements of Chemical and Physical Geology, English translation, Vol. 3, 1859, p. 200.

Details of the Replacement Beneath the Sea.—Sea water contains in solution on the average 3.5 per cent of solids. The salts present and their proportions, as averaged by Dittmar, are indicated in the following table:[275]

	PER CENT
NaCl	77.758
$MgCl_2$	10.878
$MgSO_4$	4.737
$CaSO_4$	3.600
K_2SO_4	2.465
$CaCO_3$[276]	.345
$MgBr_2$	.217

One is at once impressed by the high proportion of salts of magnesium in sea water, and it is to the action of these that dolomitization beneath the sea must be attributed. As to which of the two more abundant magnesium salts, $MgCl_2$ and $MgSO_4$, has been the most influential in the production of dolomite, nothing is definitely known, but there is some reason for believing that $MgSO_4$ is the most active agent of dolomitization. The effect of the relatively large amount of NaCl present in sea water would appear to be to repress the ionization of $MgCl_2$ and thereby to lower its efficiency greatly. In fact, experiment shows that the chloride of magnesium reacts much more feebly with $CaCO_3$ in the presence of NaCl than does the sulphate. The effect of the common sulphate ion in reducing the efficiency of $MgSO_4$ would not be nearly so great since the additional salts which possess this, $CaSO_4$ and K_2SO_4, are present in much smaller proportions.

As to the details of the reaction by which dolomite is ultimately produced by the action of the magnesium salts of the sea, it cannot be stated positively whether the double carbonate is formed directly or whether hydrous $MgCO_3$ is first formed and this subsequently combines with the $CaCO_3$ with loss of water of crystallization to form dolomite. In ordinary temperature and pressure experiments the hydrous carbonate of magnesium appears to be the normal product. It has been suggested that in time this might become dehydrated and unite with $CaCO_3$ to form dolomite. But this seems doubtful. If this were the method of replacement it does not seem probable that the re-

[275]Quoted by Grabau: Principles of Stratigraphy, 1913, p. 147.
[276]Including all traces of other salts.

action could proceed far, since the solution would become so rapidly enriched in this easily soluble constituent that equilibrium would soon be reached. If, on the other hand, we assume that the double carbonate is produced contemporaneously with replacement, the richly dolomitic limestones are easily accounted for, since under these conditions the equilibrium would not be so easily reached and the reaction might proceed until all the free $CaCO_3$ was exhausted. In short, the $MgCO_3$ produced, by combining with $CaCO_3$ as rapidly as it was formed, would be taken directly out of solution before it accumulated sufficiently to halt the forward reaction. The equilibrium would be shifted constantly towards the dolomite end of the equation. At the instant replacement takes place the $CaCO_3$ must exist in solution. It seems probable that at the time of the reaction each molecule of $MgCO_3$ formed unites with one molecule of $CaCO_3$ in solution to form the double molecule of dolomite, and that deposition then takes place. Assuming that the reaction proceeds in this manner, the equation may be written as follows:

1. $\begin{cases} MgSO_4 + CaCO_3 = MgCO_3 + CaSO_4. \\ MgCl_2 + CaCO_3 = MgCO_3 + CaCl_2. \end{cases}$

2. $MgCO_3 + CaCO_3 = CaMg(CO_3)_2.$
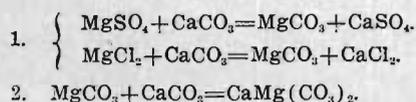
Conditions Influencing Replacement Beneath the Sea.—The more important of the factors influencing the reaction resulting in the dolomitization of limestones beneath the sea are: (1) mineral composition, (2) original content of $MgCO_3$, (3) fineness of grain, (4) porosity, (5) amount of CO_2 present, (6) temperature, (7) pressure, (8) concentration, and (9) time.

The mineral composition of the limestone is very important from the standpoint of dolomitization. It is well known that aragonite and other metastable forms of $CaCO_3$ react much more readily with chemicals than does calcite. If then a newly formed limestone consisted mainly of metastable $CaCO_3$ it would be in a very favorable condition to be dolomitized.

The presence of a small amount of $MgCO_3$ in a limestone likewise will render it more liable to dolomitization under favorable conditions.

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Fineness of grain and porosity also are important. Other things being equal the more porous a limestone and the finer its grain, the more susceptible it is to dolomitization.

To consider the influence of CO_2 on the reaction: anything which tends to render the limestone more soluble will hasten the replacement. It seems probable that the CO_2 generated by the decay of organic matter in the limestone must frequently aid considerably in taking $CaCO_3$ into solution. Limestones rich in organic remains should, therefore, be more liable to alteration than limestones poor in these, and if in a given limestone the organic matter should be more concentrated in certain local areas, we should expect these to be more easily dolomitized than the surrounding rock. This must be regarded as a possible explanation of the selective dolomitization of fucoid markings in some limestones.

Experiment shows that dolomitization proceeds most favorably at elevated temperatures, but high temperatures have never obtained over wide areas beneath the sea. The temperature of the sea, however, is not absolutely uniform, and it must be assumed that dolomitization goes on most favorably in those regions where the waters are warmest, if other conditions are the same.

Regarding the influence of pressure induced by depth on dolomitization beneath the sea, there has been some disagreement. Thus F. W. Pfaff,[277] upon finding as the result of experiment that the reaction takes place most rapidly at pressures ranging from forty to sixty atmospheres, concluded that dolomitic formations were formed at great depths corresponding to these pressures. But both Skeats and Phillipi[278] have shown this view to be untenable. There is every evidence that the dolomitization of the Paleozoic limestones has taken place at relatively shallow depths. Schuchert has estimated that these limestones were deposited at depths not exceeding 300 feet. The presence of ripple marks in dolomites such as those in the Allentown in the quarries near Allentown, Pennsylvania, and the presence of intercalated sandy layers such as those which

[277]See ante p. 311.
[278]See ante p. 281 and p. 273.

appear in the Kittatinny, Little Falls and Oneota dolomites and in many others, speaks for their shallow water origin. On the whole it does not seem probable that the replacement has taken place under pressures exceeding ten to fifteen atmospheres.

As to whether dolomitization takes place in concentrated seas or not, there has been considerable disagreement. Until recently the tendency has been to follow Dana, who intimated that the ancient dolomites were formed under conditions analogous to those which obtain when recent limestone is dolomitized in the concentrated lagoons of coral reefs. But Skeats pointed out in 1905[279] that there are cases in which the outer parts of fringing reefs facing the open ocean are dolomitized and that the dolomitization of coral reefs is not confined to the lagoons; and Phillipi soon after[280] presented evidence of recent dolomitization in the open sea. Still more recently Blackwelder[281] has given it as his opinion that the Bighorn dolomite has resulted from the progressive alteration of limestone during deposition, and that the concentration of the magnesia was not more than two or three times as great as in the present ocean, since more than this amount would have been unfavorable to the life processes of the time. There are many commendable points to this theory of progressive dolomitization at low concentrations. But if dolomitization can go on under these conditions, why are not all of our limestones dolomitic? In answer to this it might be said that the alteration takes place under unusual circumstances, possibly through the agency of certain bacteria which are not always present when limestone is deposited. But even then it is difficult to understand how magnesia could be precipitated under these conditions, since all low concentration experiments have failed to produce a precipitate of $MgCO_3$ except Leitmeier's, whose results must be regarded as questionable. Much of the field evidence also speaks against progressive dolomitization. Irregular boundaries, lateral gradations, dolomitized oölites, mottling, pseudo-interstratification effects and many other features can be accounted for only by assuming that dolomitization took place after all the beds involved were depos-

[279] See ante p. 282.
[280] See ante p. 278.
[281] See ante p. 284.

ited. When, however, a pure limestone member comformably succeeds a dolomite member known to be an alteration product and the contact line is regular and continuous over wide areas, it cannot be assumed that this relationship has resulted from the alteration of the lower bed after both beds were deposited. The "Lower Buff Beds" of northeastern Iowa, which consist of dolomite with occasional minute limestone remnants, are abruptly followed by the pure limestone of the "Lower Blue Beds" over hundreds of square miles, and the transition from one into the other takes place through only a few inches of imperfectly dolomitized limestone.

Moreover, the tendency of some limestones to be most highly dolomitic in their lower portions and to become progressively less dolomitic upwards, also must be regarded as lending support to the theory of progressive dolomitization. Orton and Peppel[282] state that the Delaware and Columbus limestones of Ohio are more dolomitic in their lower than in their upper portions.

But even if it should be positively shown that dolomitization can go on at low concentrations, all must agree that it would proceed not only much more rapidly but also more completely at higher concentrations. As to whether the ancient seas which accomplished such extensive dolomitization were more concentrated than the modern ones or not, little can yet be said. On this point we must rely solely upon inference. Steidtmann[283] has presented strong evidence to show that the ancient seas were more highly magnesian than those of today. From independent lines of reasoning based upon paleogeographic evidence the writer is also led to believe that the magnesia content of the ancient seas may have been at least temporarily greater than at present. Let us consider the conditions obtaining in a restricted interior sea from which limestone is being deposited on a great scale. Fresh quantities of lime and magnesia and other salts are being introduced into this interior sea both by influx from the open ocean and from the streams draining the land. Now lime is constantly being depleted from this inland sea by

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[282]Ohio Geol. Survey. 4th ser., Bull. 4, p. 165.
[283]Jour. Geology. Vol. 19, 1911, pp. 323 and 392.

lime-secreting organisms, while the magnesia and other salts tend to accumulate. It seems possible, then, that during a long period of limestone formation under these conditions magnesia might accumulate in considerable excess and that ere long extensive dolomitization might set in and continue until equilibrium was once more established.

Applying this theory now to the stratigraphic column, we actually find that many periods of extensive limestone formation in interior seas may be correlated with periods of extensive dolomitization. Witness the great dolomite masses of the Cambrian of the Appalachian province and of the early Ordovician and the Niagaran.

As further evidence that the early seas which accomplished extensive dolomitization may have been temporarily concentrated, attention may be called to the fact that these seas in many instances were retreating and contracting towards the last, and that unless they were freely connected with the open ocean, evaporation under arid or semi-arid conditions might give rise to a considerable increase in salinity. Such a condition would seem to apply especially well to the Niagaran Sea. Paleogeographic studies have shown that this sea became very much contracted towards the close of this epoch, and Clarke and Rudemann[284] have concluded that the Guelph fauna must have inhabited a sea of abnormally high salinity. The latter fact considered in connection with the evidence of widespread dolomitization in the later stages of the Niagaran seems significant.

The influence of the time element in dolomitization beneath the sea must be great, for we cannot escape the conviction that long periods of time must be involved in the transformation of thick beds of limestone into dolomite. Replacement beneath the sea must proceed under very stagnant conditions and the transfer of fresh magnesium salts to the scene of the reaction as well as the removal of the soluble reaction products from it must be accomplished by a process of diffusion which operates very slowly. That this diffusion must have been fairly complete, although extremely slow, is suggested by the complete-

[284]Mem. N. Y. State Museum, No. 5, p. 117.

ness to which the reaction has in many cases proceeded, and by the general absence of reaction products such as gypsum or anhydrite in the secondary dolomites.

As to the cause of pseudo-interbedding, inorganic mottling and other imperfect dolomitization effects, little definite data are available. It must be conceived that the solutions which produced these selective dolomitization phenomena permeated the rocks uniformly, but that certain layers or areas were more readily altered than others. In the case of pseudo-interbedding, several factors may have operated, viz.: variable amount of original $MgCO_3$ content; variable amount of organic matter and variable texture. The last two of these might possibly apply to inorganic mottling also. But such mottling should be regarded as a normal incipient dolomitization effect rather than a selective one. As regards the influence of textural differences in the production of pseudo-interbedding, it is believed that this has played an important part in some instances. For example, none of the coarse-grained layers of the Tribes Hill limestones at Canajoharie, New York, are more than very imperfectly altered, while many of the limestones above and below are completely changed. Textural differences, however, are far from being the whole story.

Acknowledgments.

PLATE XX.

Surface of slab of mottled Tribes Hill limestone from Palatine
Bridge, New York, two-thirds natural size. Note the rounded,
sinuous pipes of dolomite weathering in relief. Some organism
of unknown affinities appears to have exerted a selective influ-
ence upon the dolomitization.
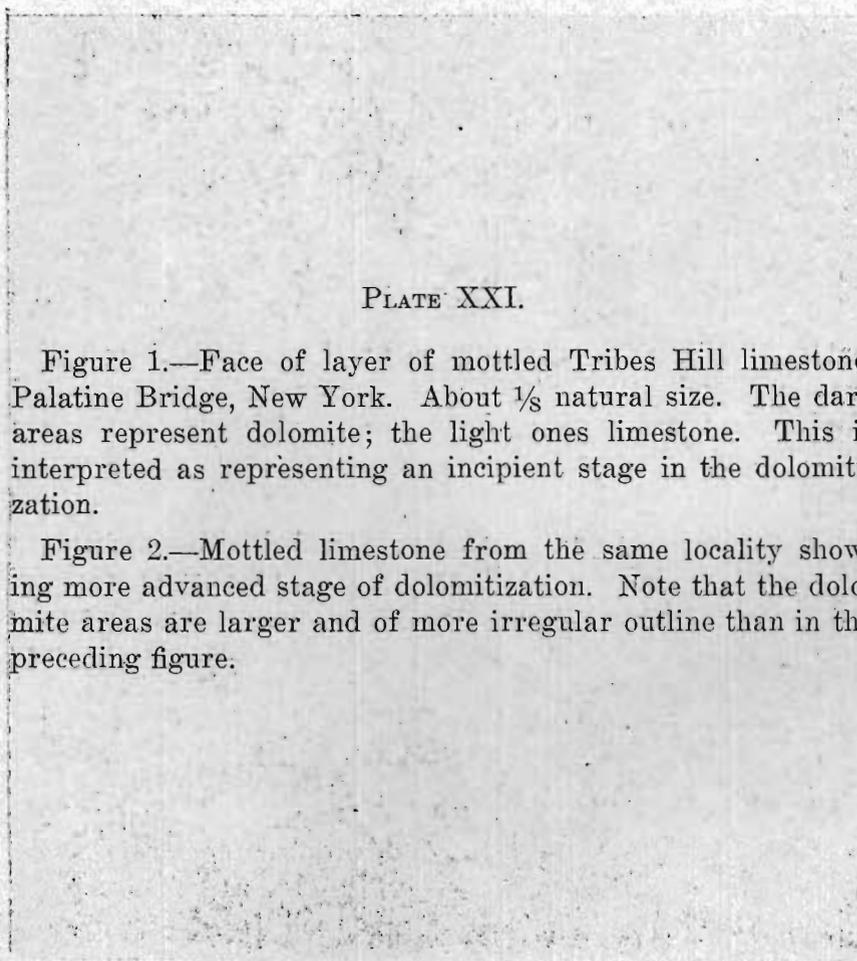
PLATE XXI.

Figure 1.—Face of layer of mottled Tribes Hill limestone, Palatine Bridge, New York. About ⅛ natural size. The dark areas represent dolomite; the light ones limestone. This is interpreted as representing an incipient stage in the dolomitization.

Figure 2.—Mottled limestone from the same locality showing more advanced stage of dolomitization. Note that the dolomite areas are larger and of more irregular outline than in the preceding figure.

FIG 1

FIG 2

PLATE XXII.

Figure 1.—Later stage of alteration of Tribes Hill limestone. The dolomite areas are larger and have begun to coalesce.

Figure 2.—The alteration nearly completed. Only very small isolated areas of limestone remain.
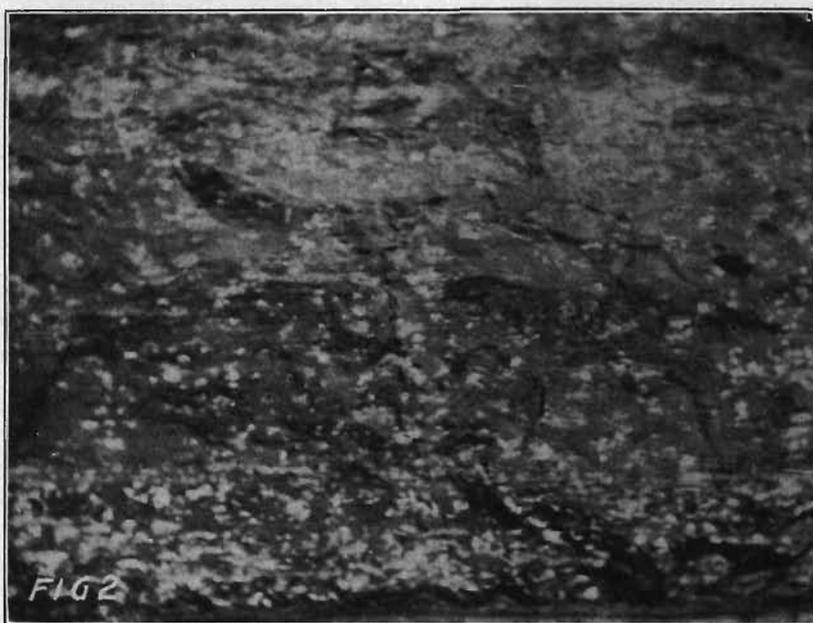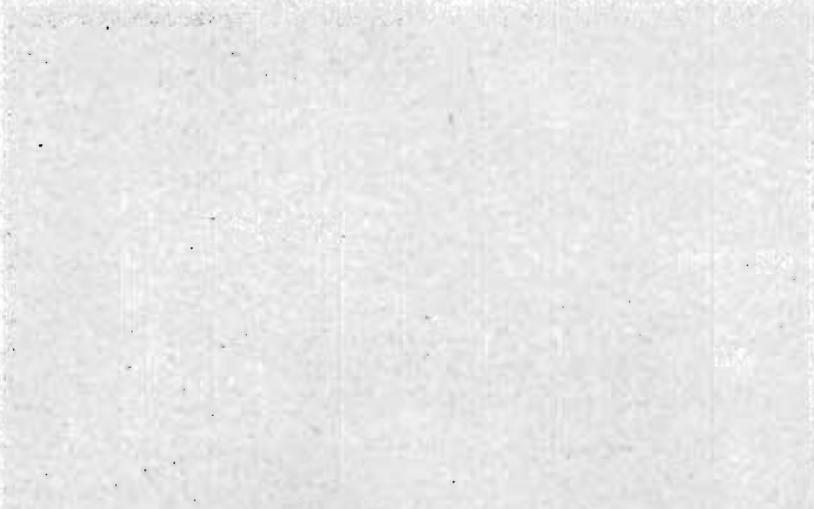
414

PLATE XXIV.

Figure 1.—Microphotograph of imperfectly altered fine-grained Devonian limestone from Portland, Iowa. X 22. The relation of calcite to dolomite was clearly brought out by staining the former, which shows dark, with Lemberg's solution. Note the tendency toward the development of zonal bands of calcite in the large dolomite crystals.

Figure 2.—Section of Cedar Valley limestone from Osage, Iowa. X 22. This shows large metacrysts of dolomite with a fine-grained groundmass of calcite. The imperfect character of the dolomite crystals is due to the presence of many minute inclusions of calcite.

Figure 3.—Section of Stonehenge limestone from Bellefonte, Pennsylvania, X 55, showing zonal growths of siderite and dolomite in a matrix of fine-grained calcite.

Figure 4. — Extremely fine-grained dolomite of unknown origin from the Jefferson City formation near Perryville, Missouri. X 41.

Figure 5.—Fine-grained dolomite known to be of secondary origin from the Fayette breccia near Bertram, Iowa. X 41. Compare with Fig. 4.

Figure 6.—Imperfectly dolomitized brecciated Saint Louis limestone from Belfast, Iowa. X 22. Some of the angular fragments of limestone have resisted alteration although the matrix is uniformly altered.
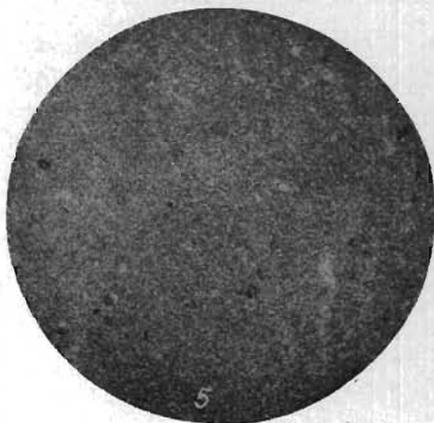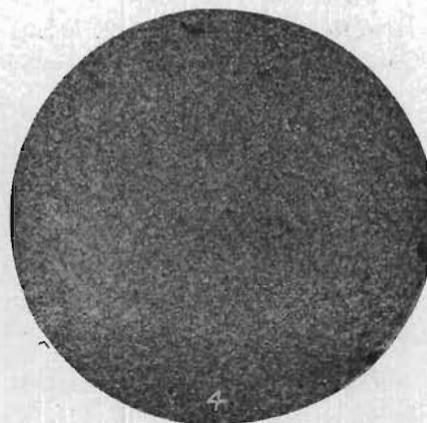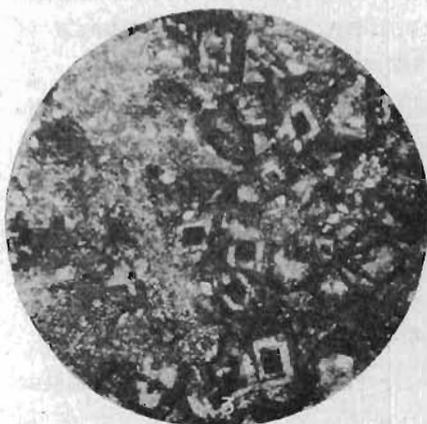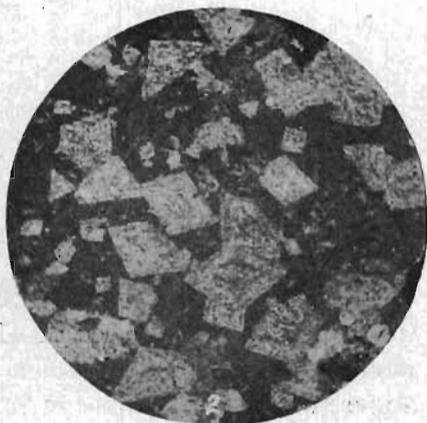
PLATE XXV.

Figure 1.—Section of mottled Tribes Hill limestone from Canajoharie, New York. X 41. Showing small limestone area partly surrounded with dolomite. A small veinlet of dolomite appears in the limestone in the upper part of the figure.

Figure 2.—Mottled Tribes Hill limestone from Palatine Bridge, New York. X 41. A minute irregular remnant of fine-grained calcite in coarser-grained dolomite.

Figure 3.—From the same section as figure 2. Observe the tongue-like extension of dolomite invading the limestone.

Figure 4.—Another area from the same sample as figure 1 showing gradational contact between limestone and dolomite areas. The dolomite crystals in the limestone area are, for the most part, very perfect but those of the dolomite area are more irregular, due to growth interference.

Figure 5.—Mottled Tribes Hill limestone from Palatine Bridge, New York. X 41. Small areas of dolomite developed in the limestone early in the progress of dolomitization.

Figure 6.—Dolomite from the Tribes Hill formation at Palatine Bridge, New York. X 41. This shows the nature of the product of more complete transformation of the limestone. No calcite remnants remain in this rock.
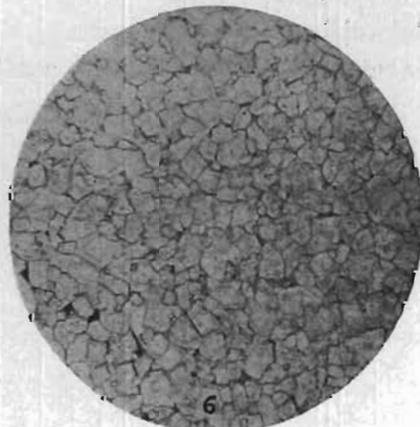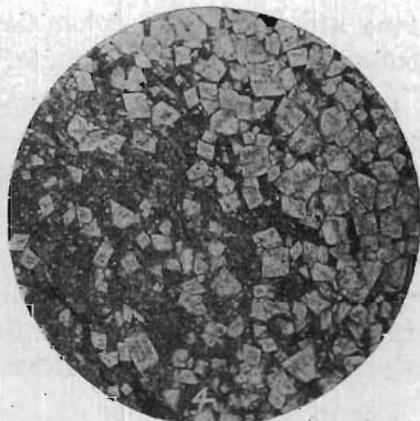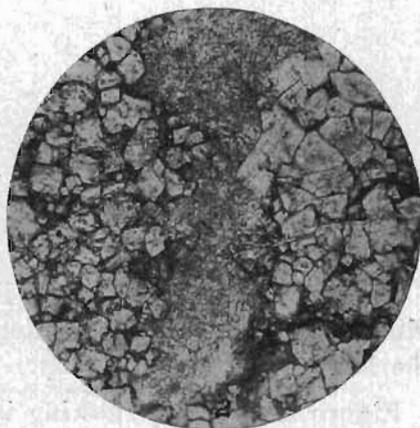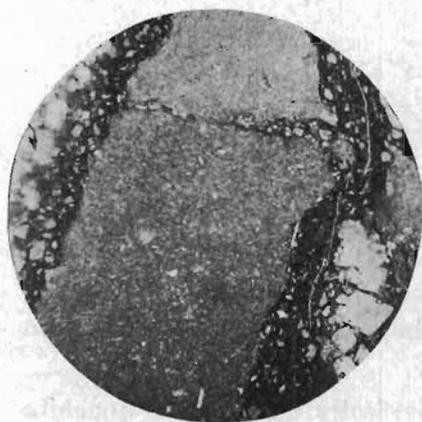
PLATE XXV.

PLATE XXVI.

Figure 1.—Mottled Plattin limestone from near Perryville, Missouri. X 22. In this section the dolomite areas grade into the limestone very gradually.

Figure 2.—Section showing imperfectly dolomitized Joachim limestone from near Bloomsdale, Missouri. X 22. The limestone areas near the dolomitic ones are filled with small disseminated crystals of dolomite.

Figure 3.—Imperfectly altered coarse-grained Chazy limestone from Chazy, New York. X 22. The small transparent rhombohedrons scattered through the section are of dolomite.

Figure 4.—Organism with calcareous tissues altered to dolomite. Cedar Valley limestone, Fairport, Iowa. X 22. The large white areas consist of calcite filling original cavities. This coarse-grained calcite resisted alteration at the time the finer-grained calcareous tissues were changed to dolomite.

Figure 5.—Section of Burlington crinoidal limestone from Chautauqua, Illinois. X 22. The rock has undergone incipient dolomitization, as is shown by the presence of the minute, transparent rhombs of dolomite scattered about through the matrix.

Figure 6.—Imperfectly altered Cedar Valley limestone from the same sample as figure 4.