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John J. Gilligan, Governor  
DEPARTMENT OF NATURAL RESOURCES  
William B. Nye, Director  
DIVISION OF GEOLOGICAL SURVEY  
Horace R. Collins, Chief

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Report of Investigations No. 86

**HIGH-CALCIUM LIMESTONE FACIES OF THE  
DEVONIAN DUNDEE LIMESTONE,  
NORTHWESTERN OHIO**

by

David A. Stith

Columbus  
1972

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# HIGH-CALCIUM LIMESTONE FACIES OF THE DEVONIAN DUNDEE LIMESTONE, NORTHWESTERN OHIO

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## ABSTRACT

A lithographic limestone facies of the Devonian Dundee Limestone is exposed in two quarries in Paulding County, Ohio, and is present in the subsurface in much of the northwestern corner of the state at depths of less than 900 feet. Samples of this facies were collected from one of the quarries and from representative water- and oil-well sample strings. The samples were analyzed for calcite, dolomite, and quartz by X-ray diffraction and for calcium, magnesium, silicon, aluminum, iron, and potassium by atomic absorption spectrophotometry.

Results of the analyses show that the facies is a high-calcium limestone. In general, calcite content is greater than 95 percent; MgO is less than 0.5 percent, SiO<sub>2</sub> is less than 1.0 percent, and Fe<sub>2</sub>O<sub>3</sub> is less than 0.1 percent.

## INTRODUCTION

### Purpose and scope

High-calcium limestone is a commodity that is becoming increasingly scarce. As the demand for pure limestone increases and the surface supplies are worked out, those deposits not now economically attractive may become minable.

At the present time a lithographic limestone facies of the Dundee Limestone is exposed in two quarries in Paulding County, Ohio (State mine numbers Pg 1 and Pg 2). In a recent report Janssens (1970) showed the distribution and thickness of the facies in the subsurface in Defiance, Williams, and parts of Fulton, Henry, and Paulding Counties. The isopach lines in figure 1 are reproduced from figure 7 of his report. The purpose of the present report is to show the mineralogical and chemical composition of this lithographic facies as determined by X-ray diffraction and atomic absorption spectrophotometry.

### Geologic setting

The Dundee Limestone of northwestern Ohio is Middle Devonian in age. It is underlain by the Detroit River Group and overlain by the Traverse Group.

The Detroit River Group in the study area is undifferentiated. It is sublithographic to finely crystalline light- to medium-gray, grayish-brown, and brown dolomite and sandy dolomite, laminated and pelletal in part.

The Dundee Limestone can be divided into two units. The lower Dundee is sandy sucrosic light-gray and light-brown dolomite and limestone with abundant chert. The upper Dundee is fossiliferous medium- to coarse-grained light-gray, yellowish-gray, and medium-brown limestone. In the study area the basal portion of the upper Dundee is a sublithographic to lithographic very light-gray, medium-gray, and grayish-brown limestone, pelletal in part. The outcrop of the lithographic facies is limited to a portion of Paulding County and extreme southeastern Defiance County. The glacial overburden in this area is mainly ground moraine and

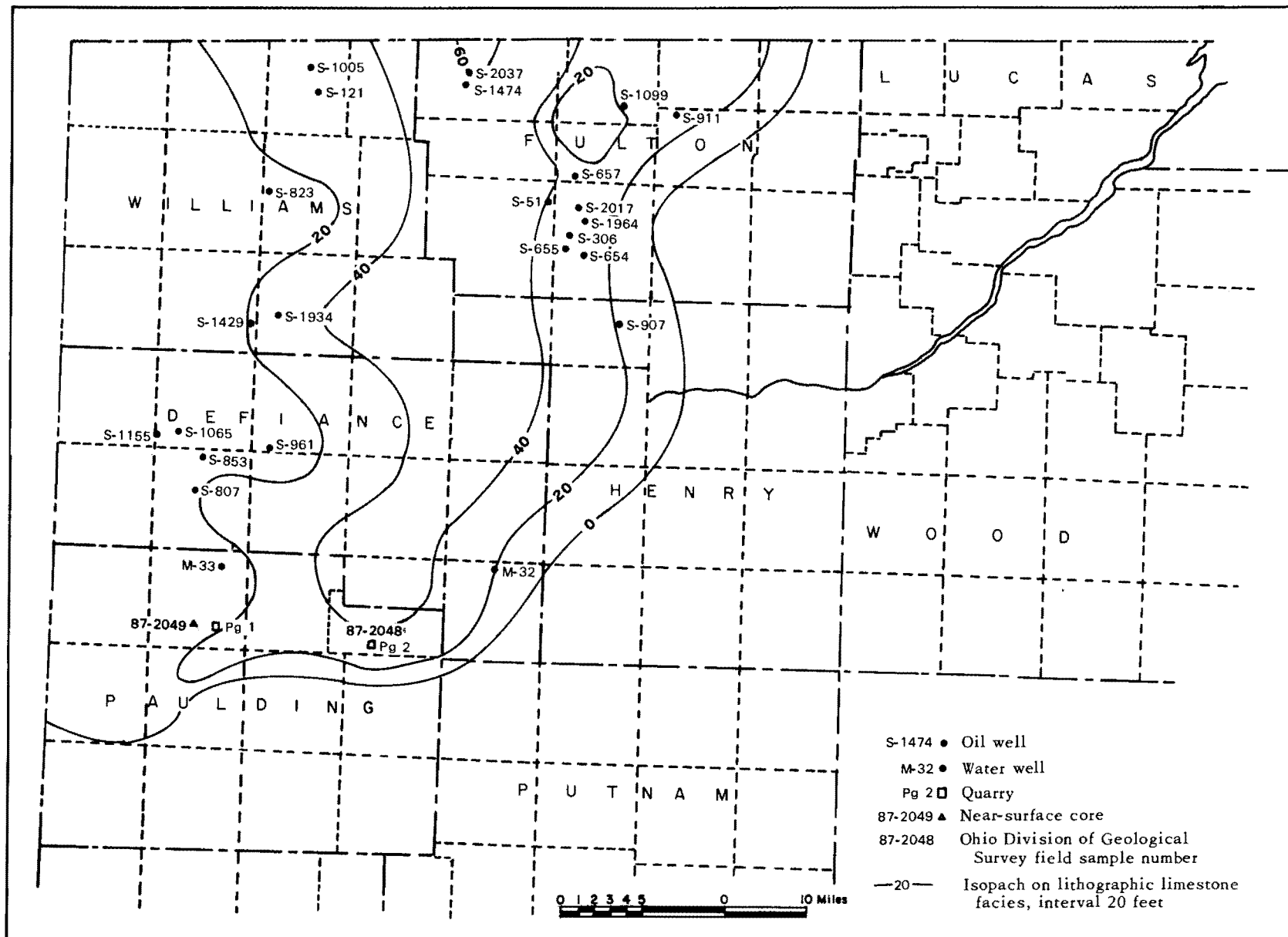


FIGURE 1.—Locations of sampling sites; isopachs on lithographic limestone facies from Janssens (1970).

lacustrine silt and clay and ranges from 15 to 70 feet. Maximum depth to the facies is about 900 feet in Williams County.

In northwestern Ohio the Traverse Group consists of the Silica Formation and the Tenmile Creek Dolomite. The Silica Formation, overlying the Dundee, is interbedded fossiliferous grayish-brown limestone and shale. The Tenmile Creek Dolomite is fine- to medium-grained light-yellowish-gray dolomite with abundant chert. In much of Williams County and the northwestern part of Defiance County, limestone predominates and the Traverse is undifferentiated (Janssens, 1970).

#### Acknowledgments

The author would like to express his appreciation to the managements of those quarries contributing samples to this study. The well sample descriptions were done by Dr. Adriaan Janssens for his study on the Devonian of northwestern Ohio (Janssens, 1970). Mr. Norman Knapp assisted the author in the chemical analyses.

## PROCEDURE

### Sample collection

Samples collected for the study were of two types: grab samples (100- to 300-gm) from a quarry and a near-surface core and smaller samples (1- to 50-gm) from water- and oil-well drill cuttings (fig. 1). The quarry samples were from Auglaize Township (Pg 2), where the rock was sampled at 1-foot intervals, starting at the base of the lithographic facies. The quarry in Crane Township (Pg 1) was not sampled but quarter-splits at approximate 1-foot intervals were obtained from a 2½-inch core drilled half a mile west of the quarry.

All pertinent water- and oil-well sample strings on file at the Ohio Division of Geological Survey were examined, but only those considered reliable and with sufficient material to allow for adequate sampling were used in the study. Laboratory samples for chemical and X-ray analysis were split from the drill cuttings and material for analysis was obtained by one of three methods, depending on particle size and on degree of contamination of the samples: (1) lithographic material was handpicked from coarse gross drill samples, (2) lithographic material was handpicked from the coarse-sieve (+35 mesh) split of fine gross drill samples, or (3) the contaminants were removed by handpicking from gross drill samples. Seventy-one samples were collected from 22 oil-well and 2 water-well strings. An additional 48 samples were collected from the core and quarry in Paulding County. Descriptions and depths of the samples are given in the appendix.

### Quantitative X-ray analysis

The determination of the mineralogical composition of a rock by X-ray diffraction has become commonplace. The methods primarily used determine either the ratio of the minerals in a rock from the ratio of their diffraction intensities or the absolute percentages of minerals in a rock from the ratios of their diffraction intensities to that of an internal standard (Azároff and Buerger, 1958; Cullity, 1956; Fisher, 1968; Gulbrandsen, 1960; Runnells, 1970).

All of the samples were analyzed by quantitative X-ray diffraction. The internal standard method was used with reagent-grade  $\text{CaF}_2$  (fluorite) as the standard. The rock was ground to less than 85 mesh by hand or by a micropulverizer, depending on the amount of sample. Each sample was prepared for X-ray analysis by mixing approximately 0.75 gm of sample with sufficient  $\text{CaF}_2$  to produce a mixture of 75 percent sample and 25 percent  $\text{CaF}_2$ . The mixture was pulverized for 10 minutes in a SPEX #5100 mixer/mill, then mixed with approximately 5 ml of water and subjected to ultrasonic disaggregation for 2 minutes. The resulting slurry was transferred by eyedropper to three glass slides and dried at 105°C. Standards for the calibration curves were prepared in the same way as the samples. Reagent-grade  $\text{CaCO}_3$ , high-purity Guelph Dolomite, and a pulverized single crystal of quartz were used to prepare the calibration standards.

TABLE 1.—X-ray instrument settings

Goniometer speed	1° 2θ/min
Chart speed	30 in/hr.
Range	26°-31.5° 2θ
Radiation	CuKα
Filter	Ni
Power	35 kv, 20 ma
Recorder full scale	2000 cps

The samples and standards were run on a Norelco diffractometer at the settings shown in table 1. Table 2 lists the diffraction peaks utilized for the analyses. Peak heights were taken as the intensity measurement instead of peak area or integrated intensity. The average intensity was calculated for each of the four peaks in table 2 and the mineral-to-fluorite intensity ratios  $I_C/I_F$ ,  $I_D/I_F$ , and  $I_Q/I_F$  were calculated for each stand-

TABLE 2.—X-ray diffraction peaks used in quantitative analysis

Mineral	$d\text{Å}$	{hkl}	Degrees 2θ
$\text{SiO}_2$	3.343	{101}	≈26.6
$\text{CaF}_2$	3.153	{111}	28.3
$\text{CaCO}_3$	3.035	{211}{10·4}	29.43
$\text{CaMg}(\text{CO}_3)_2$	2.886	{211}{10·4}	≈30.95



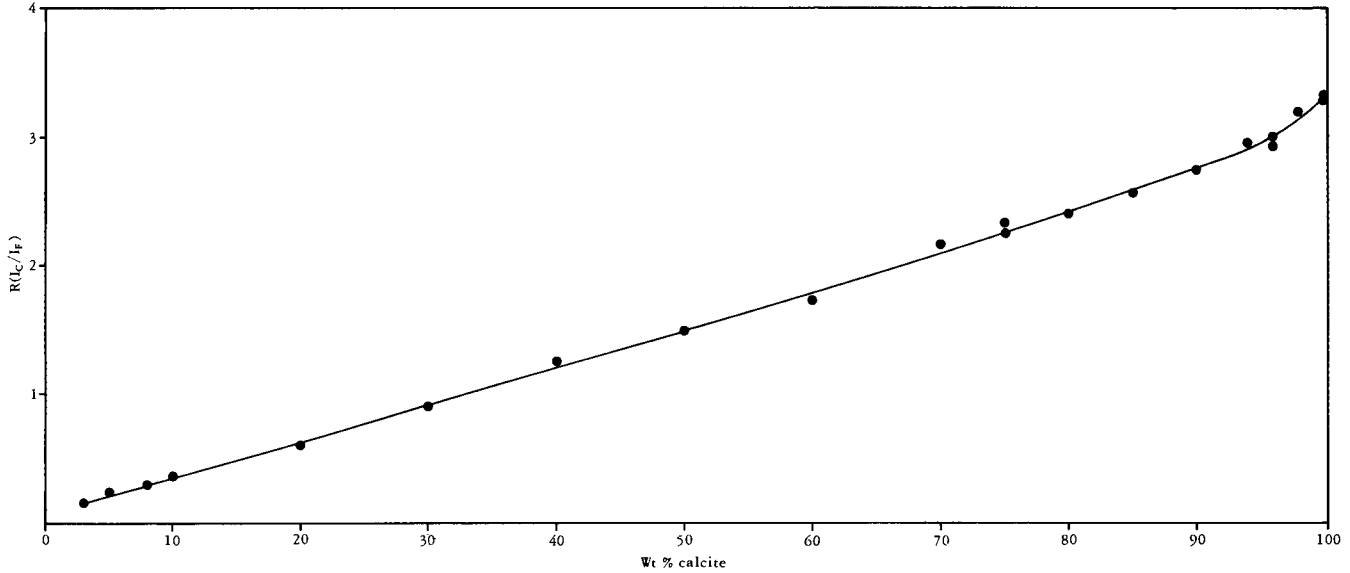


FIGURE 2.—X-ray calibration curve for calcite.

ard. Calibration curves (figs. 2, 3, 4) for the three minerals were prepared by plotting the ratios versus the weight percent of the mineral in the original standard mixture (before addition of  $\text{CaF}_2$ ). Mineral-to-fluorite ratios were then calculated for each sample and the mineral percentages obtained from the calibration curves.

#### Chemical analysis

Following X-ray analysis the samples were analyzed by atomic absorption spectrophotometry for calcium, magnesium, silicon, aluminum, iron, and potas-

sium. Individual core and quarry samples were combined into 3- to 6-foot composite samples. Individual well samples with sufficient material were run separately. Where drill cuttings were sparse the chemical samples were obtained by combining cuttings from several or all of the drilling intervals sampled within the lithographic facies. Forty-one samples were analyzed chemically.

The sample decomposition method was adapted from a procedure described by Katz (1968) for aluminum and silicon analysis. Approximately 0.5 gm of sample was weighed to the nearest 0.1 mg into a 50-ml nickel crucible and fired in a muffle furnace at 750°C for a

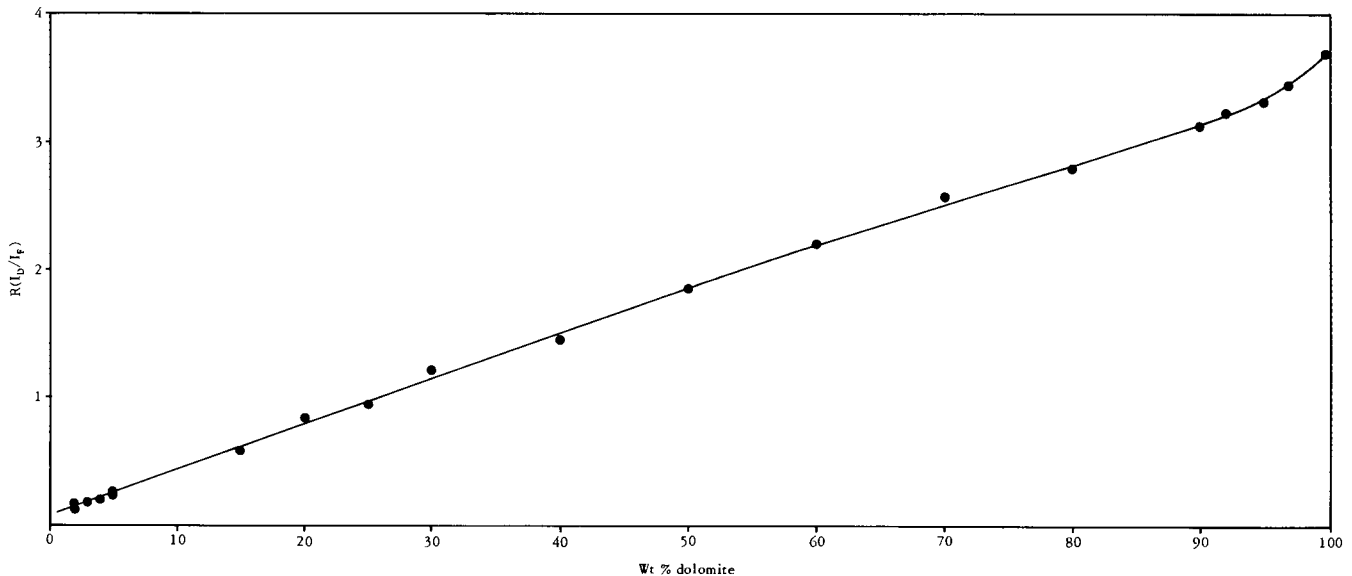


FIGURE 3.—X-ray calibration curve for dolomite.

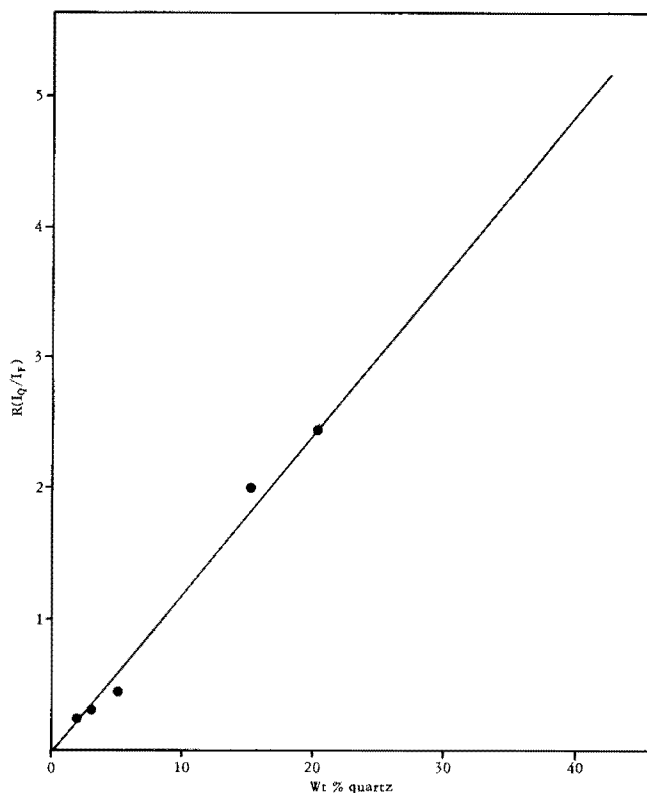


FIGURE 4.—X-ray calibration curve for quartz.

minimum of 2 hours to calcine the carbonates. After cooling, approximately 1 gm of NaOH pellets was added, and the crucible was heated slowly over a Meker burner. After the NaOH melted, the heat was increased slightly until the melt was homogeneous. After cooling, the fused material was dissolved in a small amount of warm water and transferred to a 100-ml volumetric flask with repeated washing. Five ml of concentrated HCl and 20 ml of a 5 percent solution of lanthanum in 25 percent HCl were added to the flask. After cooling to room temperature, the solution was diluted to volume with distilled water. Silicon (except for one sample diluted 1 to 2), aluminum, iron, and potassium were run on the above solution. For calcium the initial solution was diluted 1 to 100 and for magnesium it was diluted 1 to 10, 1 to 100, or 1 to 200, depending on the amount of magnesium present.

Calcium, magnesium, iron, and potassium stock solutions were commercial standards with a concentration of 1,000 ppm of the element. The aluminum stock solution was prepared by dissolving 1.0 gm of aluminum in a small amount of HNO<sub>3</sub>, diluting to 1 liter, and standardizing by an oxinate precipitation method. Silica stock solution was prepared from a clear single crystal of quartz, handground to less than 200 mesh. One gm of the silica was fused with 6 gm of NaOH and diluted to 1 liter. The solution was standardized as quinoline silicomolybdate.

Working standards for silicon, aluminum, iron, and

potassium were prepared as a single set of solutions, shown in table 3. Calcium standards were 25, 20, 15, 10, 5, and 0 ppm with an HCl and lanthanum content diluted to 0.1 and 0.01 percent, respectively. Magnesium standards were 2.0, 1.5, 1.0, 0.5, 0.2, and 0 ppm with blank levels for calcium of 200 ppm, for HCl of 1 percent, and for lanthanum of 0.1 percent.

TABLE 3.—AAS standard solutions

Standard solution	ppm					Percent	
	Si	Al	Fe	K	Ca	HCl	La
A	65.5	30	15	7	2000	10	1
B	46.8	20	10	5	2000	10	1
C	28.1	10	5	3	2000	10	1
D	18.7	5	3	2	2000	10	1
E	9.4	2	1	1	2000	10	1
F	0	0	0	0	2000	10	1

Chemical analyses were made with a Perkin-Elmer model 303 atomic absorption spectrophotometer with recorder readout module and 0-10 mv recorder. Single-element hollow-cathode lamps were used for all analyses. Silicon and aluminum were determined in a nitrous oxide-acetylene flame, the remaining elements in an air-acetylene flame. Standard operating parameters (Perkin-Elmer Corp., 1968) were used for all analyses except that on calcium. Due to the extremely high calcium content of the samples the burner head was turned perpendicular to the light path. This permitted the use of the 1 to 100 dilution instead of a 1 to 1,000 dilution. Ten to 12 samples were run at a time. A limestone standard (G. F. Smith #401) was included in each batch of samples as a control check.

#### X-ray solid-solution analysis

Fourteen of the samples were checked by X-ray diffraction for solid solution in the calcite. Numerous papers have been published dealing with the relationships between  $d$ -spacings and composition of the rhombohedral carbonates (Fisher, 1968; Goldsmith and Graf, 1958; Goldsmith, Graf, and Joensuu, 1955; Graf, 1961; and Rosenberg, 1963). There is a direct relationship between the size of the unit cell (and therefore the interplanar  $d$ -spacings) and the composition in a given solution series. The methods used to demonstrate this relationship involve plotting the molecular percentage of the carbonate in question versus the  $d$ -spacing or  $2\theta$  angle of a given plane, the unit cell constant ( $a_0$  or  $c_0$ ), the difference in  $d$ -spacing or  $2\theta$  angle of a plane of the sample and of a pure end-member of the series, or the difference in  $d$ -spacing or  $2\theta$  angle of a plane of the sample and a plane of an internal standard. The consensus of the cited references is that, although the change in spacing of a given reflection is not a straight line join between two end-members,

## HIGH-CALCIUM LIMESTONE FACIES OF THE DUNDEE LIMESTONE

TABLE 4.—Comparison of calcite, dolomite, and quartz by X-ray and chemical analysis

Sample number <sup>1</sup>	X-ray analysis			Chemical analysis (computed from elements)					
	Sample interval <sup>2</sup> (ft)	Calcite (%)	Dolomite (%)	Quartz (%)	Proportion of sample in composite	Sample interval (ft)	Calcite (%)	Dolomite (%)	SiO <sub>2</sub> (%)
M-32	130-140	99.8			1	130-150	97.54	0.91	0.36
	140-150	100.0			1				
M-33	100-120	96.5				100-120	97.36	0.99	0.26
S-51	450-455	95.6 <sup>3</sup>				455-475	97.44	0.99	0.28
	455-465	100.0			1				
	465-475	99.3		0.7	1				
	475-480	99.9							
	485-490	98.3		1.0					
S-121	850-856	97.6		1.0		856-867	96.99	1.59	0.62
	856-861	98.8		1.2	1				
	861-867	99.4		1.0	1				
S-306	432-438	99.8			1	432-466	98.24	0.99	0.32
	438-443	96.1			1				
	443-450	99.7			1				
	450-457	96.3			1				
	457-466	97.3		0.7	1				
S-654	411-417	99.3				411-427	97.9	1.0	
	417-427	97.9							
	427-435	98.0							
S-655	415-420	95.6			1	415-445	98.04	0.91	0.34
	420-425	98.2			1				
	425-430	94.4 <sup>4</sup>			1				
	430-435	98.2			1				
	435-440	97.5		1.3	1				
	440-445	95.7		1.2	1				
S-657	485-515	97.6		1.1		485-515	98.27	1.06	1.16
	515-520	94.0 <sup>5</sup>							
S-807	237-246	99.5		0.7		246-256	97.59	0.99	0.30
	246-256	97.4							
S-823	692-703	94.8		0.9		692-703	95.56	1.82	0.90
	703-720	97.6		1.0					
S-853	223-249	99.5				223-249	97.76	0.91	0.62
S-907	310-315	95.6				315-320	97.31	2.35	0.34
	315-320	97.2	1.0						
	320-325	94.9 <sup>5</sup>							
	325-330	95.4							
	330-335	99.3		0.9					
	335-340	98.5		1.2					
S-911	570-576	98.7		0.7		570-576	96.82	1.52	0.36
	576-586	99.8		0.9		576-586	97.74	1.36	0.58
S-961	207-214	98.0	2.2	1.1		207-214	94.32	3.64	0.64
S-1005	838-842	98.9		1.6	1	838-876	97.42	1.52	1.09
	842-850	99.8		1.1	1				
	850-866	100.0		1.0	1				
	866-876	97.5		1.2	1				
	876-890	99.8		0.9					
S-1065	330-340	93.8	5.0	0.8		330-340	91.88	6.45	0.60

## RESULTS

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TABLE 4.—Comparison of calcite, dolomite, and quartz by X-ray and chemical analysis—Continued

Sample number <sup>1</sup>	X-ray analysis			Chemical analysis (computed from elements)						
	Sample interval <sup>2</sup> (ft)	Calcite (%)	Dolomite (%)	Quartz (%)	Proportion of sample in composite	Sample interval (ft)	Calcite (%)	Dolomite (%)	SiO <sub>2</sub> (%)	
S-1099	670-680	98.9	2.3	1.0		670-680	94.21	4.55	1.09	
	680-690	98.2		1.4		680-690	95.70		2.12	1.26
	690-700	97.2		1.3		690-700	94.13		2.66	1.13
S-1155	315-322	97.2		1.3						
S-1429	375-380	100.0				375-380	99.05	0.83	0.26	
	380-390	98.0				380-390	97.69		0.91	0.34
	390-400	98.2				390-400	97.44		0.91	0.41
S-1474	660-670	99.1				660-670	98.77	0.76	0.49	
	670-680	99.2		0.8		670-680	98.15		0.83	0.43
	680-690	98.2				680-690	97.59		0.76	0.41
	690-700	100.0		1.0		690-700	98.53		0.83	0.60
	700-710	98.9		0.8		700-710	98.44		0.91	0.45
S-1934	370-380	100.0		1.0	1	370-380+				
	380-390	95.5		1.0						
	390-400	97.5		1.1	1	390-400	97.26	1.82	0.96	
S-1964	460-480	91.5	5.7	1.3		460-480	92.27	6.37	1.11	
S-2017	460-470	96.5	1.0		1	460-470+				
	470-485	95.6		0.8						
	485-495	100.0			1	485-495	97.81	1.82	0.28	
S-2037	679-688	100.0			1					
	688-695	98.6			1	679-705	97.49	0.99	0.43	
	695-705	97.5			1					
	715-721	96.7		0.5	1					
	721-733	96.3		1.0	1	715-733	97.05		1.44	0.56
87-2048	29.5	98.0								
	29.0	98.2			1					
	28.0	100.0			1					
	27.0	99.7			1	26-29	97.40	0.83	0.45	
	26.0	96.1			1					
	25.0	100.0		1.1	1					
	24.0	99.5			1					
	23.0	100.0		1.0	1	21-25	97.62	0.76	0.43	
	22.0	99.0			1					
	21.0	98.0			1					
	20.0	97.7			1					
	19.0	96.3			1					
	18.0	97.0			1	16-20	97.58	0.83	0.26	
	17.0	96.5			1					
	16.0	97.8			1					
	15.0	98.7	0.5	0.9	1					
	14.0	96.7			1					
13.0	99.0				1	11-15	96.43	1.14	0.47	
12.0	99.0			0.9	1					
11.0	95.7			1.3	1					
87-2048	10.0	95.6		1.4	1					
	9.0	100.0			1					
	8.0	100.0		0.7	1	6-10	98.38	0.83	0.56	
	7.0	94.9		1.0	1					
	6.0	100.0		1.0	1					

TABLE 4.—Comparison of calcite, dolomite, and quartz by X-ray and chemical analysis—Continued

Sample number <sup>1</sup>	X-ray analysis				Chemical analysis (computed from elements)				
	Sample interval <sup>2</sup> (ft)	Calcite (%)	Dolomite (%)	Quartz (%)	Proportion of sample in composite	Sample interval (ft)	Calcite (%)	Dolomite (%)	SiO <sub>2</sub> (%)
87-2049	5.0	83.6	13.7	1.9	2	0-5	43.94	50.46	4.21
	4.0	43.8	58.8	1.7	2				
	3.0	10.0	87.5	0.7	2				
	2.0	10.2	85.8	1.0	2				
	1.0	60.0	39.5	1.0	2				
	0.0	71.5		28.7	1				
	73.0	99.4		1.0	1	73-78	97.43	0.83	0.43
	74.0	95.8		0.9	2				
	75.0	98.9			2				
	76.0	98.7			2				
	77.0	95.2		1.3	2				
	78.0	100.0			2				
	79.0	99.3			1	79-84	98.57	0.61	0.45
	80.0	95.8		0.9	1				
	81.0	99.5			1				
	82.0	100.0		1.0	1				
	83.0	97.7		1.0	1				
	84.0	97.3		1.2	1				
	85.0	96.7			1	85-89.25	97.02	1.82	0.45
86.0	98.4		1.0	1					
87.0	99.1		0.9	1					
88.5	97.5	0.5		1					
89.25	97.2	4.0		1					

<sup>1</sup>M-32, Ohio Division of Water sample number; S-51, Ohio Division of Geological Survey well sample number; 87-2048, Ohio Division of Geological Survey field sample number.

<sup>2</sup>Drilling depth intervals for wells; footage above base of formation for surface sample (2048); core depth for core sample (2049).

<sup>3</sup>Sample too small.

<sup>4</sup>Standard fluorite weight incorrect.

<sup>5</sup>Portion of sample lost from grinding vial.

the departure from a straight line is small.

The  $\{11\bar{2}\}\{03\cdot0\}$  peaks for the samples, pure calcite ( $64.655^\circ 2\theta$ ), and dolomite ( $67.425^\circ 2\theta$ ), were scanned on a Norelco diffractometer with a goniometer speed of  $\frac{1}{4}^\circ 2\theta$  per minute and a chart speed of 15 inches per hour. The  $K\alpha_1$  peak was used in all cases. The molecular percentages of  $\text{CaCO}_3$  in calcite and dolomite were plotted versus  $d_{\{11\bar{2}\}}$  and the molecular composition of the samples determined from the resultant straight line. Although other elements, notably iron and manganese, can enter into the series, all of the material in solid solution was considered to be magnesium.

## RESULTS

### Quantitative X-ray analysis

Results of the X-ray analyses are shown in table 4. The detection limits for dolomite and quartz were

2 percent and 1 percent, respectively. Values lower than this are due to averaging the X-ray data for the three slurry mounts for each sample: dolomite and/or quartz were not detected in all three mounts in some samples.

During the course of the analyses three problems arose. In some instances the amount of sample available in a well interval was significantly less than the 0.75 gm weight selected for the mixtures. When such a sample was pulverized for 10 minutes the grinding effects were quite different than on larger samples; calcite, dolomite, and quartz totals were commonly much less than 100 percent. Also, the grinding vials at times showed a tendency to leak, causing either effects similar to those caused by small sample size or enhanced X-ray peaks due to incomplete pulverizing. Analyses obviously showing either or both of these effects were rejected and rerun where sufficient sample was available.

The final problem was due to the nature of X-radiation. The copper  $K\beta$  rays were largely, but not com-

TABLE 5.—Chemical analysis data

Sample number <sup>1</sup>	Sample interval <sup>2</sup> (ft)	Chemical analysis						Sample number <sup>1</sup>	Sample interval <sup>2</sup> (ft)	Chemical analysis					
		CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O			CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O
M-32	130-150	54.92	0.20	0.36	0.06	0.03	0.02	S-1429	375-380	55.74	0.18	0.26	0.04	0.03	0.02
M-33	100-120	54.85	0.22	0.26	0.05	0.03	0.02		380-390	55.00	0.20	0.34	0.06	0.03	0.02
S-51	455-475	54.89	0.22	0.28	0.05	0.04	0.02		390-400	54.86	0.20	0.41	0.07	0.03	0.03
S-121	856-867	54.82	0.35	0.62	0.10	0.03	0.04	S-1474	660-670	55.56	0.16	0.49	0.09	0.08	0.04
S-306	432-466	55.34	0.22	0.32	0.07	0.04	0.02		670-680	55.24	0.18	0.43	0.08	0.07	0.04
S-655	415-445	55.20	0.20	0.34	0.08	0.04	0.03		680-690	54.90	0.16	0.41	0.08	0.07	0.03
S-657	485-515	55.38	0.23	1.16	0.05	0.04	0.02		690-700	55.45	0.18	0.60	0.12	0.07	0.05
S-807	246-256	54.97	0.22	0.30	0.04	0.04	0.02		700-710	55.42	0.20	0.45	0.07	0.04	0.03
S-823	692-703	54.09	0.40	0.90	0.16	0.06	0.06	S-1934	370-380+	55.04	0.40	0.96	0.15	0.04	0.06
S-853	223-249	55.04	0.20	0.62	0.14	0.06	0.05		390-400						
S-907	315-320	55.22	0.51	0.34	0.07	0.06	0.02	S-1964	460-480	53.63	1.39	1.11	0.20	0.28	0.06
S-911	570-576	54.71	0.33	0.36	0.09	0.18	0.03								
	576-586	55.17	0.30	0.58	0.08	0.14	0.03	S-2017	460-470+	55.35	0.40	0.28	0.07	0.05	0.02
S-961	207-214	53.95	0.80	0.64	0.04	0.02	0.01		485-495						
S-1005	838-876	55.04	0.33	1.09	0.20	0.07	0.08	S-2037	679-705	54.92	0.22	0.43	0.08	0.07	0.03
S-1065	330-340	53.44	1.41	0.60	0.10	0.04	0.04		715-733	54.81	0.32	0.56	0.09	0.04	0.04
S-1099	670-680	54.16	0.99	1.09	0.14	0.14	0.05	87-2048	26-29	54.82	0.18	0.45	0.13	0.06	0.05
	680-690	54.26	0.46	1.26	0.18	0.17	0.06		21-25	54.92	0.16	0.43	0.09	0.09	0.03
	690-700	53.55	0.58	1.13	0.15	0.14	0.05		16-20	54.92	0.18	0.26	0.07	0.05	0.03
									11-15	54.37	0.25	0.47	0.11	0.05	0.04
									6-10	55.36	0.18	0.56	0.08	0.02	0.03
									0-5	39.96	11.03	4.21	0.19	0.14	0.07
								87-2049	73-78	54.83	0.18	0.43	0.07	0.02	0.03
									79-84	55.41	0.13	0.45	0.03	0.02	0.01
									85-89.25	54.92	0.40	0.45	0.06	0.04	0.03

<sup>1</sup>M-32, Ohio Division of Water sample number; S-51, Ohio Division of Geological Survey well sample number; 87-2048, Ohio Division of Geological Survey field sample number.

<sup>2</sup>Drilling depth intervals for wells; footage above base of formation for surface sample (2048); core depth for core sample (2049).

pletely, removed by a nickel filter. The angular position for the calcite  $K\beta$  reflection for  $\{211\}$  is within  $0.2^\circ 2\theta$  of the  $\{101\}$   $K\alpha$  reflection of quartz. Since the calcite content of most of the samples was quite high there was generally a minor  $K\beta$  calcite peak. In several instances there was a problem in determining whether the peak in the vicinity of  $26.5$ - $26.6^\circ 2\theta$  was a calcite  $K\beta$  or a quartz  $K\alpha$  reflection. This probably accounts for the differences in silica values obtained from X-ray analyses relative to those obtained from chemical analyses.

#### Chemical analysis

The results of the chemical analyses, calculated as oxides, are shown in table 5. Values for silica and for calcium and magnesium, calculated as calcite and dolomite with all of the magnesium in dolomite, are shown in table 4. Table 6 shows the means and standard deviations of analyses of the limestone standard

(G. F. Smith #401).

The biggest source of inaccuracy in the chemical analyses is the large amount of calcium in the samples and the dilution (1 to 100) required to run the analyses. An error of 0.3 percent calcium in a sample, when calculated as the carbonate, would amount to nearly 0.75 percent of the rock. Differences in the dolomite values obtained by X-ray analysis and by chemical analysis are explained in the following section.

TABLE 6.—Limestone standard (G. F. Smith #401), analytical results

	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O
Ingamells and Suhr (1967)	50.07	3.60	2.09	0.22	0.199	0.06
Mean, this study	49.47	3.63	2.11	0.23	0.198	0.06
$\sigma$	0.343	0.063	0.047	0.0063	0.0090	0.0017

TABLE 7.—Solid-solution data

Sample number <sup>1</sup>	Sample interval (ft)	Solid solution		Chemical analysis	Difference between chemical analysis and solid solution values	Quantitative X-ray analysis
		Mol % MgCO <sub>3</sub> in calcite	Wt % MgCO <sub>3</sub> in calcite	Wt % MgCO <sub>3</sub>		Wt % MgCO <sub>3</sub>
S-961	207-214	0.85	0.70	1.66	0.96	1.01
S-1065	330-340	0.45	0.36	2.95	2.59	2.29
S-1099	670-680	1.00	0.81	2.08	1.27	1.05
S-1964	460-480	0.65	0.51	2.91	2.40	2.61
S-2017	460-470+ 485-495	1.00	0.84	0.83	-0.01	0.23
S-807	246-256	0.45	0.38	0.45	0.07	-
S-823	692-703	1.15	0.96	0.83	-0.13	-
S-911	570-576	0.25	0.21	0.69	0.48	-
S-1099	680-690	0.85	0.70	0.97	0.27	-
S-1429	375-380	0.25	0.21	0.38	0.17	-
S-1474	660-670	0.45	0.38	0.35	-0.03	-
S-1474	680-690	0.10	0.08	0.35	0.27	-
S-1474	690-700	0.25	0.21	0.38	0.17	-
S-2037	715-733	0.45	0.38	0.66	0.28	-

<sup>1</sup> Ohio Division of Geological Survey well sample number.

#### X-ray solid-solution analysis

Chemical analysis shows minor magnesium in all samples, a result not confirmed by X-ray analysis. In those samples in which small amounts of dolomite were detected by X-ray, the dolomite contents calculated from chemical analysis are greater by approximately those same small amounts than the figures calculated for samples that showed no dolomite by X-ray. This relationship prompted the solid-solution study. The 14 samples checked included most of those that showed minor amounts of dolomite by X-ray analysis. All samples checked showed evidence of solid solution in calcite; figures ranged from 0.10 to 1.15 mol percent as MgCO<sub>3</sub>, with most of the samples between 0.45 and 1.00 mol percent. Within the limits of experimental error, the amounts of magnesium found in solid solution account for the differences in dolomite content determined by X-ray and by chemical analysis (table 7). In those samples showing no dolomite by X-ray analysis, the differences in MgCO<sub>3</sub> content shown by chemical analysis and by solid-solution determination were less than the detection limit for dolomite.

#### SUMMARY

The lithographic facies in the upper Dundee Limestone as described by Janssens (1970) is a high-calcium limestone. Chemical and X-ray analysis of well samples suggests that the high purity characteristic of the facies at the outcrop is characteristic also of the unit in the subsurface in the area of study. In gen-

eral, MgO content is less than 0.5 percent, SiO<sub>2</sub> is less than 1.0 percent, and Fe<sub>2</sub>O<sub>3</sub> is less than 0.1 percent.

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## APPENDIX

*Sample descriptions*

Sample number <sup>1</sup>	Sample interval <sup>2</sup> (ft)	Method of sampling <sup>3</sup>	Sample description
M-32	130-140	A	Limestone, very light-tannish-gray, lithographic. Limestone, medium-gray, medium- to coarse-grained; 25%
	140-150	A	Limestone, light-tannish-gray, lithographic to sublithographic. Limestone, medium-gray, medium- to coarse-grained; 25%
M-33	100-120	A	Limestone, light-tannish-gray, lithographic; pelletal in part. Dolomite, very light-brown, microcrystalline; trace
S-51	450-455	A	Limestone, very light-brownish-gray, medium-grained to dense to lithographic
	455-465	C	Limestone as above
	465-475	C	Limestone as above
	475-480	A	Limestone as above
	480-485		Samples missing
	485-490	A	Limestone as in sample from 450 to 455 feet
S-121	850-856	B	Limestone, very light-yellowish-brown to yellowish-gray to medium-brown, lithographic to sublithographic
	856-861	B	Limestone as above, predominantly very light yellowish brown. Limestone, medium-grained, dense; trace
	861-867	B	Limestone as above
	867-875		Limestone as above, not sampled because particles too small
S-306	432-438	B	Limestone, very light-gray, lithographic
	438-443	A	Limestone as above
	443-450	B	Limestone as above
	450-457	B	Limestone as above
	457-466	A	Limestone as above
S-654	411-417	A	Limestone, light-yellowish-gray to very light-grayish-brown, lithographic
	417-427	A	Limestone as above, light to medium brown in part
	427-435	A	Limestone as above
S-655	415-420	A	Limestone, very light-gray to brownish-gray, lithographic
	420-425	A	Limestone as above, light brown
	425-430	A	Limestone as above
	430-435	A	Limestone as above
	435-440	A	Limestone as above
	440-445	C	Limestone as above
S-657	485-515	A	Limestone, very light-brownish-gray, sublithographic, fossiliferous
	515-520	A	Limestone as above, light brown, in part lithographic. Limestone, light-yellowish-gray, medium-grained, microcrystalline, sandy (rounded fine-grained sand); minor
S-807	237-246	A	Limestone, very light-brownish-gray, sublithographic to medium-grained; minor amount sandy (fine-grained sand)
	246-256	A	Limestone, very light-brown to grayish-brown, fine- to medium-grained, lithographic to sublithographic to dense; sandy as above in part
S-823	692-703	A	Limestone, very light- to light-brown, fine- to medium-grained, slightly sandy (fine-grained sand). Limestone, light-brown, lithographic; 10%
	703-720	A	Limestone, lithographic as above. Limestone, light- to dark-brown, fine- to coarse-grained, pelletal and pseudo-oolitic(?), dense
S-853	223-249	A	Limestone, very light-gray to light-tannish-gray to very light-brown, lithographic to sublithographic. Limestone, medium-brown to dark-brownish-gray, medium- to coarse-grained, argillaceous

*Sample descriptions—Continued*

Sample number <sup>1</sup>	Sample interval <sup>2</sup> (ft)	Method of sampling <sup>3</sup>	Sample description
S-907	310-315	A	Limestone, very light-gray to yellowish-gray, lithographic to medium-grained to dense (predominantly lithographic)
	315-320	A	Limestone as above
	320-325	A	Limestone as above
	325-330	A	Limestone as above, trace of sulfur
	330-335	A	Limestone as in sample from 310 to 315 feet, 95%, probable contaminant. Dolomite, very light-brownish-gray to yellowish-gray, fine- to medium-grained, finely to medium-crystalline; sandy (subangular very fine- to fine-grained sand); good interporosity
	335-340	A	Limestone and dolomite as above, trace of sulfur
S-911	570-576	C	Limestone, very light-gray, lithographic to sublithographic
	576-586	C	Limestone as above
S-961	207-214	A	Limestone, very light- to light-brown, lithographic to sublithographic
S-1005	838-842	B	Limestone, very light-grayish-brown to medium-brown, lithographic to medium-grained (predominantly lithographic)
	842-850	B	Limestone, light- to medium-brown, sublithographic to micrograined, dolomitic
	850-866	B	Limestone, very light-brownish-gray to gray to light-grayish-brown, lithographic to coarse-grained, dense; pelletal in part
	866-876	B	Limestone as above
	876-890	B	Limestone as above. Limestone and dolomite, very light-grayish-brown to medium-brown, fine- to medium-grained, finely crystalline, sucrosic; 20%
S-1065	330-340	B	Limestone, very light-grayish-brown to yellowish-brown to light-brown, lithographic to coarse-grained, dense; heavy trace of selenite and sulfur. Dolomite, light-gray, dark-gray-mottled (burrow?), microcrystalline; trace
S-1099	670-680	C	Limestone, very light-yellowish-brown, dense, predominantly sublithographic; fine- to medium grained in part
	680-690	C	Limestone as above, very light grayish brown
	690-700	C	Limestone as above
S-1155	315-322	B	Limestone, very light-grayish-brown, lithographic to medium-grained, dense. Limestone, very light-brown, coarse-grained, pelletal; trace
S-1429	375-380	A	Limestone, very light-gray and very light- to medium-brown, fine-grained, fossiliferous, coralline in part. Limestone, very light-gray to brownish-gray, lithographic
	380-390	A	Limestone as above
	390-400	B	Limestone, light-brown to grayish-brown to very light-brownish-gray, lithographic to dense. Limestone as above, fine grained; trace
S-1474	660-670	C	Limestone, very light-grayish-brown, lithographic
	670-680	C	Limestone as above
	680-690	C	Limestone as above
	690-700	A	Limestone as above. Limestone, fine- to medium-grained; trace
	700-710	A	Limestone as above, predominantly light brown
S-1934	370-380	A	Limestone, light-grayish-brown to medium-brown, lithographic to sublithographic. Limestone, very light-brownish-gray, fine-grained and finely crystalline, sucrosic; trace
	380-390	A	Limestone as above, predominantly very light brownish gray, oolitic and pelletal
	390-400	A	Limestone as above
S-1964	460-480	C	Limestone, light-yellowish-gray to very light-brownish-gray, lithographic
S-2017	460-470	C	Limestone, very light-brownish-gray to grayish-brown, lithographic
	470-485	B	Limestone as above
	485-495	A	Limestone as above

## Sample descriptions—Continued

Sample number <sup>1</sup>	Sample interval <sup>2</sup> (ft)	Method of sampling <sup>3</sup>	Sample description	
S-2037	679-688	A	Limestone, light-brown to brownish-gray, lithographic to sublithographic	
	688-695	A	Limestone as above	
	695-705	A	Limestone as above	
	705-715		Sandstone, light-gray to greenish-gray, fine-grained, glauconitic; argillaceous in part. Dolomite, very light- to medium-brown and light-yellowish-gray, fine- to coarse-grained, microcrystalline, sandy. Chert, white, fossiliferous; trace. Shale, medium-green; trace. Not sampled, Sylvania Sandstone(?) samples out of place?	
	715-721	A	Limestone as in sample from 679 to 688 feet. Dolomite and shale as above; sand fine to coarse grained, rounded. Sandstone, trace	
	721-733	A	Limestone, very light-brown, fine- to medium-grained, dense, lithographic	
87-2048	29.5	D	Limestone, light-gray- and gray-mottled, lithographic	
	29.0	D	Limestone, very light-gray, sublithographic	
	26-28	D	Limestone, light-gray to very light-gray, lithographic	
	19-25	D	Limestone, very light-gray, lithographic; bird's-eye structures	
	12-18	D	Limestone, light-gray to very light-gray, lithographic; some stylolites and bird's-eye structures	
	8-11	D	Limestone, light-tannish-gray, lithographic to sublithographic	
	6-7	D	Limestone, light-gray, lithographic, stylolitic	
	4-5	D	Limestone, dolomitic, light-tannish-gray to tannish-gray, finely crystalline	
	2-3	D	Dolomite, tan to brown, finely crystalline, faintly sucrosic	
	1	D	Limestone, brown to light-brownish-gray, dolomitic, sublithographic; laminated in part	
	0	D	Limestone, brown, finely crystalline, silty	
	87-2049	73.0	E	Limestone, brown, sublithographic
		74.0	E	Limestone, grayish-brown, lithographic
75.0		E	Limestone, light-brownish-gray, lithographic	
76.0		E	Limestone, light-grayish-brown, lithographic, faintly laminated, stylolitic	
77.0		E	Limestone, grayish-brown, sublithographic, bird's-eye structures	
78.0		E	Limestone, brownish-gray, lithographic	
79.0-80.0		E	Limestone, grayish-brown and light-grayish-brown, lithographic, laminated	
81.0		E	Limestone, light-grayish-brown, lithographic	
82.0-85.0		E	Limestone, grayish-brown, pelleral	
86.0		E	Limestone, brownish-gray, sublithographic	
87.0		E	Limestone, grayish-brown, lithographic	
88.5		E	Limestone, brown, sublithographic	
89.25		E	Limestone, light-gray, lithographic	

<sup>1</sup>M-32, Ohio Division of Water sample number; S-51, Ohio Division of Geological Survey well sample number; 87-2048, Ohio Division of Geological Survey field sample number.

<sup>2</sup>Drilling depth intervals for wells; footage above base of formation for surface sample (2048); core depth for core sample (2049).

<sup>3</sup>A, handpicked from gross drill sample; B, handpicked from coarse sieve (+35 mesh) split of drill sample; C, gross drill sample minus handpicked contaminants; D, grab sample from quarry wall at 1-foot intervals; E, quarter split of 2 $\frac{1}{8}$ -inch core, 2- to 4-inch pieces.