High-Brightness Limestones in Indiana

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Introduction

After the reorganization of the Indiana Geological Survey in the late 1940's, geologists in the Industrial Minerals Section began a systematic investigation of commercial limestone and dolomite deposits. At each active quarry and at many abandoned quarries and prominent natural exposures, geologists measured sections and collected samples for chemical determinations by the Geochemistry Section. Of the the thousands of analyzed samples on file, we selected more than 450 high-calcium limestones for a new study on brightness.

Use of high-purity, high-brightness limestone for filler or whiting applications in the United States in 1979 amounted to more than 1.3 million tons with a value of $32.5 million (18), but none was produced in Indiana despite its central location with respect to markets and premium prices paid for bright stone. Because we felt that some of Indiana's high-calcium limestones (greater than 95 percent calcium carbonate) had properties that would allow them to be used for fillers, we began brightness measurements to determine their suitability.

Thick units of carbonate rocks are abundant near the surface in Indiana. Numerous chemical analyses have shown that high-purity limestones of significant thickness occur in the Paoli Limestone (Late Mississippian), Ste. Genevieve, and Salem Limestones (Middle Mississippian); the Muscatatuck Group (Middle Devonian); and the Wabash Formation (Middle and Late Silurian) (Figure 2). Details on brightness will be reported for specific examples of limestones from Carroll, Orange, and Harrison Counties (Figure 1).

Limestone Fillers

Significant amounts of high-purity, bright limestones are used in plastics (20 percent), rubber (15 percent), paints (20 percent), putty and joint fillers (20 percent), adhesives and floor coverings (20 percent), and paper (<5 percent), where the limestone acts as inexpensive filler, extender, or pigment and to a small degree as a coating (6, 9, 10, 11). As with most industrial minerals, cost is important; location of the deposit with respect to market plays a large role in overall cost of the products. Much filler comes from Georgia, New England, Texas, and Illinois; some Indiana high-calcium limestone, if of suitable brightness, would appear to be favorably situated to markets. Distribution of raw materials and specifications for this use as fillers are outlined by Cummins (7), Key (12), Severinghaus (16), and Wilson and Skinner (19).

Besides very fine particle size, chemical purity and high brightness are essential for fillers (Table I). Generally there should be high amounts of calcite or dolomite (>95 percent) and low amounts of $MgCO_3$ (<2 percent for limestones), silica (<1 percent), iron oxide ($<.1$ percent), and alumina (<1 percent). Brightness is an important property of fillers; most limestones have brightness >85 percent, although brightness for materials in floor coverings can be in the low 80-percent range. Goodwin and Baxter (8) suggested that limestones with brightness >70 percent should be considered as potential materials for fillers. Other properties, such as particle size and shape, oil-absorption characteristics, and flow properties may also be important (3, 7, 19).

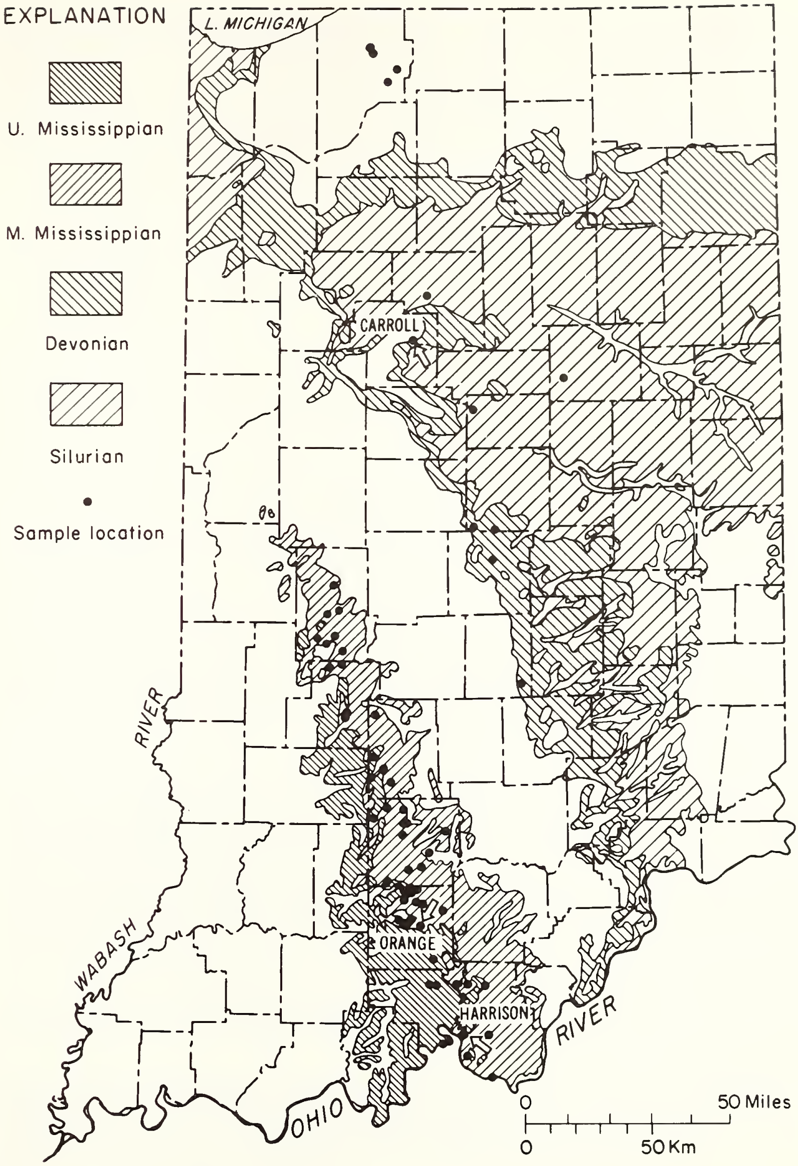

FIGURE 1. *Map of Indiana showing bedrock distribution of geologic units that contain high-purity carbonate rocks and sample sites.*

Brightness

Samples were finely ground (80-90+ percent passing a 325-mesh nylon screen), and the resulting powders were pressed into pellets by using a metal ring,

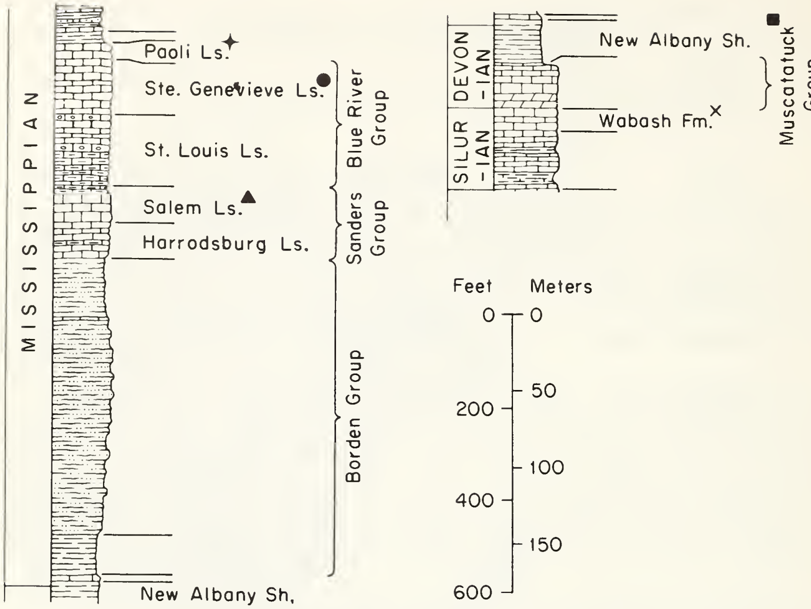

FIGURE 2. *Generalized columnar section showing rock units occurring near surface that contain high-purity carbonate rocks. Symbols refer to sample sites shown in Figure 3.*

plunger, and a smooth, flat glass plate (Figure 4). Pellets were placed on the search unit of a Photovolt 670 reflectance meter, and the amount of light reflected from the powder, relative to a powdered $BaSO_4$ standard furnished by Kodak (99 percent reflectance) and an enamel standard furnished by the manufacturer, was determined. Measurements were made by using blue, green, and amber filters, so that tristimulus color and whiteness, or yellowness, indices could be determined.

TABLE I. *Specifications for commercial fillers as reported by four companies (A, B, C, and D).*

FILLER SPECIFICATIONS				
	A	B	C	D
$CaCO_3$ (%)	98.0-99.8	98.0	90.96	54.0
$MgCO_3$ (%)	Trace	1.50	0.60	44.0
SiO_2 (%)	–	0.60	1.40	0.5
Fe_2O_3 (%)	0.02	0.05	0.08	0.1
Al_2O_3 (%)	0.10	0.08	0.50	0.4
BRIGHTNESS	88–96	95-98	87-91	94

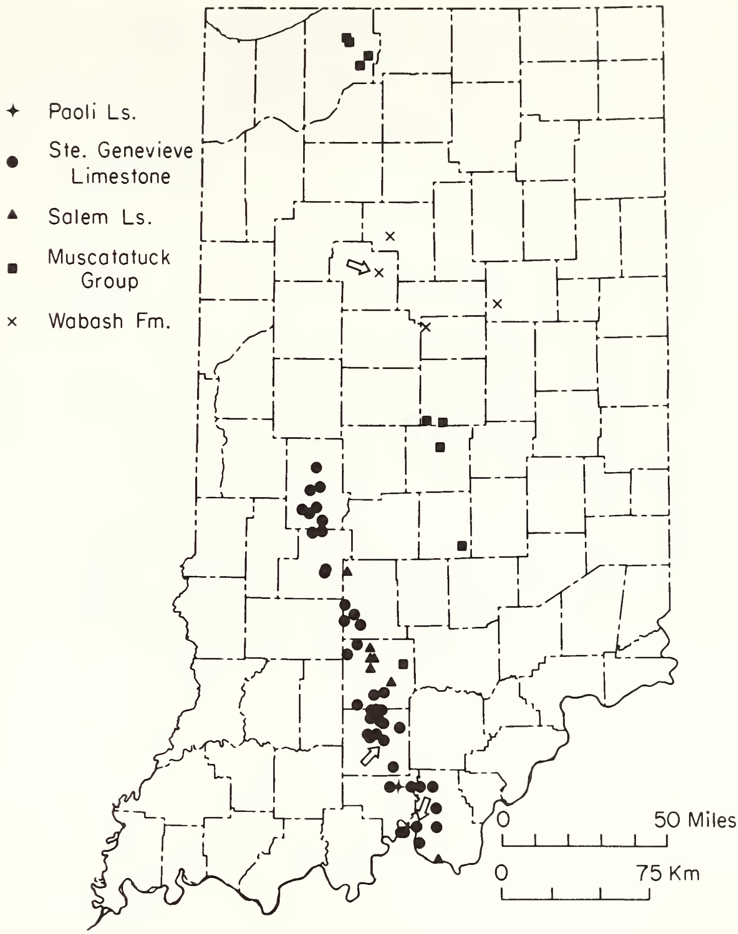

FIGURE 3. *Map showing sample locations. Symbols indicate stratigraphic units shown in Figure 2. Open arrows refer to site locations mentioned in text in Carroll, Orange, and Harrison Counties (north to south).*

This method is a modified version of Pulverized Limestone Association standard 5-68T. Brightness is reported as dry reflectance and was reproducible to ± 0.1 percent on single pellet and about ± 0.5 percent on different pellets. Our measurements compared favorably with other laboratories but showed wider variance because different equipment and filters were used.

A summary of the reflectance measurements for Indiana limestones (Figure 5) clearly shows that some limestones have relatively high brightness values. The samples with highest reflectance values came from the Ste. Genevieve Limestone, which ranged from 67 to 88 percent brightness and averaged 81 percent, and from the Wabash Formation, which ranged from 72 to 91 percent brightness and averaged 82 percent. Disappointingly, but not unexpected, low values were found for the St.

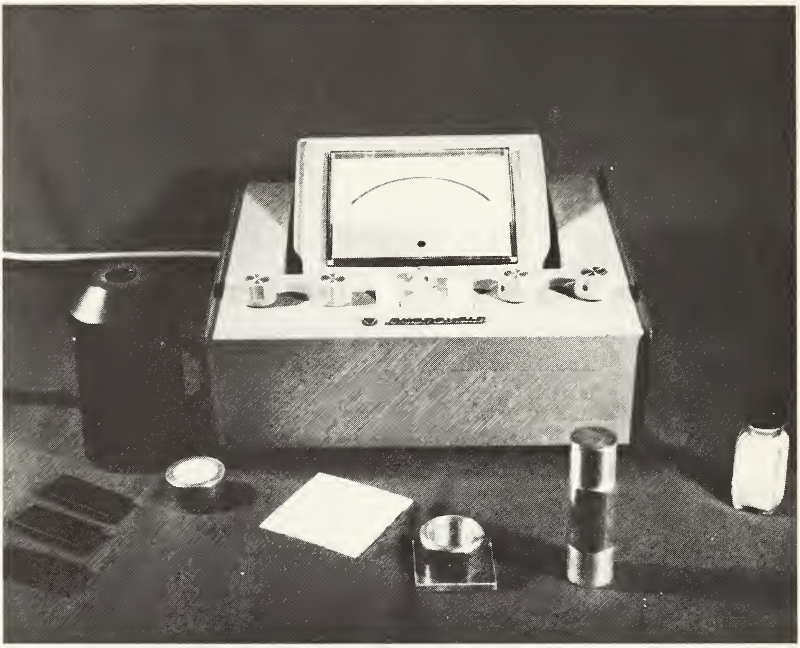

FIGURE 4. *Equipment used to measure brightness. Powder was pressed into pellets, and reflectance through three filters was measured by comparing with standards.*

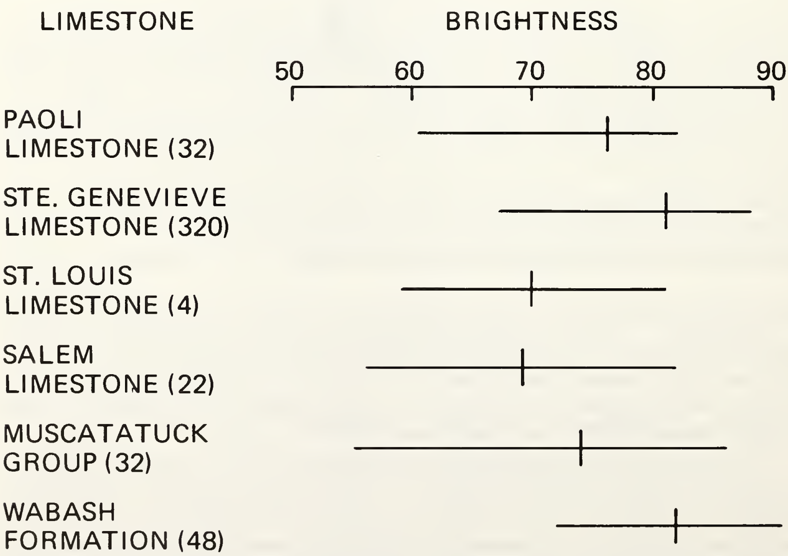

FIGURE 5. *Range and average brightness values of high-purity carbonate rocks from Indiana. Numbers in parentheses indicate number of samples.*

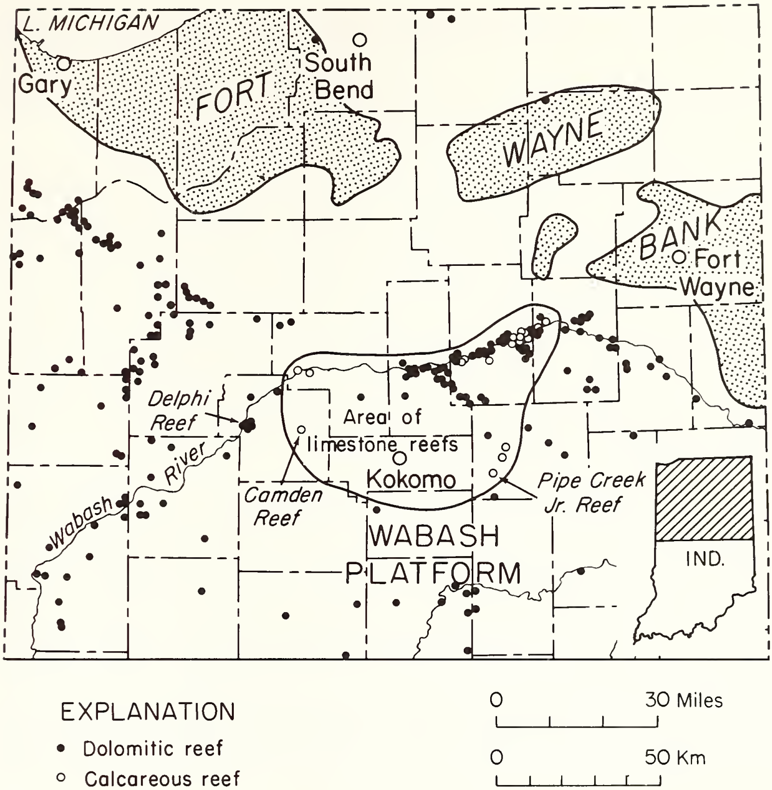

FIGURE 6. *Map of northern Indiana showing locations of known reefs and area of limestone reefs. From Ault and Carr, Figure 3 (2).*

Louis and Salem Limestones, which ranged from 56 to 82 percent brightness and averaged 69 percent. Relatively low values also were obtained for carbonate rocks from the Muscatatuck Group, which ranged from 56 to 82 percent brightness and averaged 74 percent, and from the Paoli Limestone, which ranged from 61 to 82 percent and averaged 76 percent.

Limestones of Silurian and Devonian Age

Thick high-calcium limestone is present in several formations of Devonian age in southeastern and northern Indiana and in a few of the hundreds and possibly thousands of reefs that grew on the broad Wabash Platform that extended through much of northern and central Indiana during Silurian time (Figure 6; 17). Most of the reefs have been dolomitized, such as the reef complex at Delphi and reefs of the Ft. Wayne Bank, but several limestone reefs are known in an area that includes parts or all of several counties in north-central Indiana (1, 2).

The highest brightness values we have recorded for Indiana rocks have come from samples of the more than 250 feet of high-calcium limestone that has been test drilled in a large reef of Silurian age near Camden in Carroll County. A similar reef in southeastern Grant County at the Pipe Creek Jr Quarry also contains thick high-purity limestone that has commercial potential for high-brightness products. The above two reefs are about 1 mile in diameter at their largest dimensions at the bedrock surface and are more than 300 feet thick. They are mushroom-shaped with their smallest dimensions at their bases in rocks of Middle Silurian age.

Lithologies of the limestone in both reefs are similar. They are mostly high-calcium limestones that are light gray to white and that contain less than 2 percent noncarbonate minerals. The high-purity limestone consists of skeletal material, much of it fragmental, that has been tightly cemented with clear to white sparry calcite in reef-flank beds. Although parts of the reefs are dolomitic limestone or dolomite, large reserves of high-calcium limestone have been test drilled in the Camden and Pipe Creek Jr reefs. The dolomitic parts of the reefs are mostly far-flank beds that are gradational with dolomitic interreef beds, but a test core drilled near the center of the Camden reef showed fine-grained gray dolomite in the upper part of the core. Some dolomitic limestone has also been drilled in parts of the flank rock of the Pipe Creek Jr reef. The dolomitization has been partly related to the original porosity of the dolomitized beds (1, 13).

Of the 17 known reefs in Indiana containing limestone, only the Camden and Pipe Creek Jr reefs have large commercial reserves of high-calcium limestone. The other reefs are a few hundred feet to less than a quarter of a mile in diameter at the bedrock surface and commonly less than 100 feet thick. Although these reefs might be profitably exploited with mobile crushing plants, reserves of any individual reef would probably not be sufficient for a permanent processing plant. Besides, many of the smaller reefs contain some gray to tan dolomite and significant amounts of impurities, especially on the weathered outcrops of the reefs.

Ault and Carr (2) presented results of chemical analyses of limestone from 15 reefs in north-central Indiana and discussed methods of exploration in an area of known limestone reefs (Figure 6), an area that would also have the greatest potential for future sources of high-brightness limestone.

High-calcium limestone is present in several rock formations of Devonian age. These include the Jeffersonville and North Vernon Limestones in southeastern Indiana and the Traverse Formation in northern Indiana. Thick high-purity limestones have been determined to occur in numerous places in these rocks (14, 15); these rocks range from light gray to tan, but our measurements show no reflectance values that exceed 86 percent. Our data suggest that limestones of Devonian age do not have exceptional brightness and have limited commercial potential. Beneficiation might increase the brightness of Devonian limestones, but we have no data to confirm this assumption.

Dolomites and dolomitic limestones of Silurian and Devonian age range from gray to brown and are somewhat darker than the high-calcium limestones, but our tests have not included dolomitic rocks, and a comprehensive evaluation of the brightness of these rocks has yet to be made. Light-gray dolomitic rocks are found in some formations, notably the Laurel Member of the Salamonie Dolomite (Silurian) and the Louisvile Limestone (Silurian), and a very light buff high-purity dolomite from the Salamonie Dolomite has been quarried for use as filler at the Meshberger Bros. Stone Corp. Quarry near Portland, Jay County.

Weighted averages of chemical analyses for the Camden limestone reef show a great thickness of limestone suitably pure for fillers. Brightness values plotted against depth (Figure 7) indicate that substantial thicknesses of a very bright limestone also occur in parts of the reef. Values were not determined for all samples.

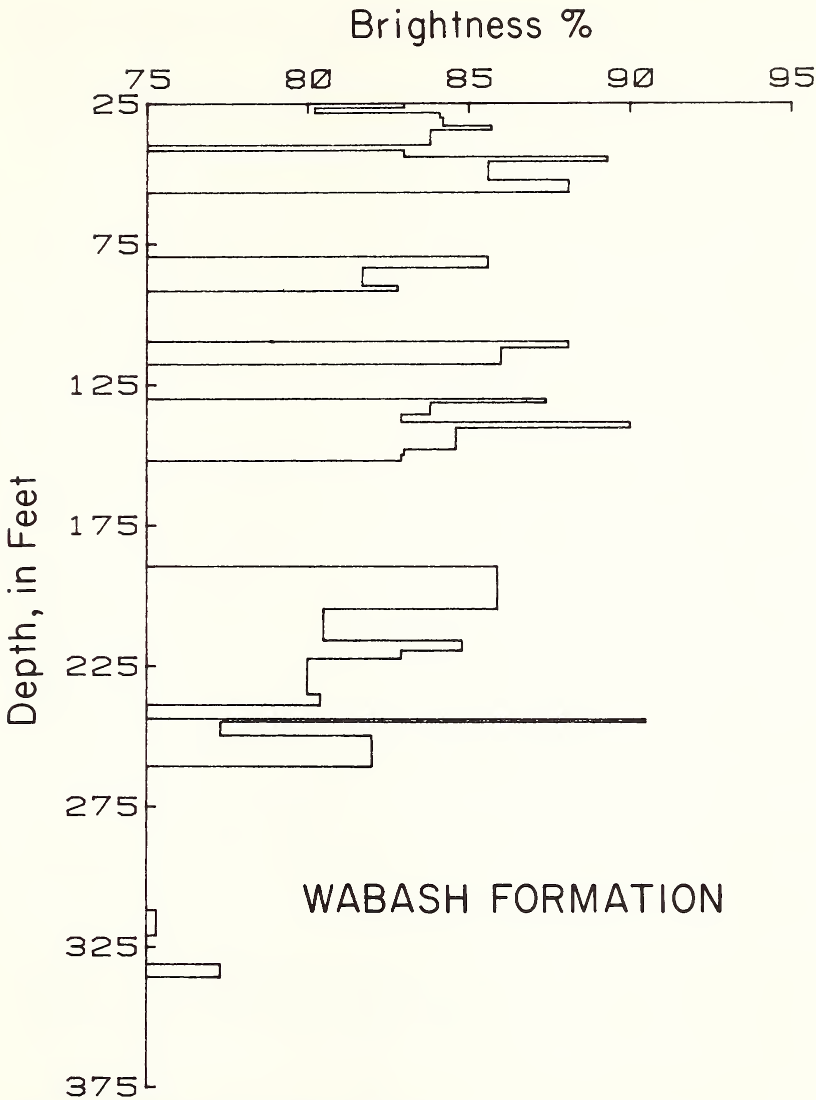

FIGURE 7. *Distribution of brightness values with depth in a limestone reef of the Wabash Formation in Carroll County.*

Limestones of Mississippian Age

Chemical analyses indicate high-calcium limestones in the Paoli, Ste. Genevieve, St. Louis, and Salem Limestones (5, 14). Samples from the Salem and St. Louis Limestones generally gave relatively low values for brightness (Figure 5). But no beneficiation was attempted on any limestones, and simple treatment might yield improved brightness results. Rocks of the Ste. Genevieve Limestone have good potential for filler raw material with brightness values near 90 percent and an average of 81 percent reflectance. The Paoli Limestone also has some potential.

High-calcium limestone in beds more than 10 feet thick occur in the Harrodsburg, Salem, and Ste. Genevieve Limestones of Middle Mississippian age and in the Paoli, Beaver Bend, Beech Creek, and Glen Dean Limestones of Late Mississippian age. Only those in the Salem, the Ste. Genevieve, and the Paoli are thought to be extensive enough to be commercially important.

The dimension-stone facies of the Salem Limestone, which occurs in beds as much as 75 feet thick in the Bedford-Bloomington District, has consistently tested to be about 97 percent $CaCO_3$ and 1.5 percent $MgCO_3$ (14), but its gray and buff colors, due to small amounts of iron oxide and organic matter, reduce its desirability for high-brightness limestone. Brightness measurements for the Salem have never exceeded 82 percent and have averaged only 69 percent, which suggests that the Salem has limited commercial importance. We have not attempted beneficiation techniques to increase brightness.

The Paoli and Ste. Genevieve Limestones, which crop out along a belt from central Putnam County to Crawford and Harrison Counties along the Ohio River, are grouped together because they contain similar lithologies (4). Although high-calcium limestone of several textural types is found in these formations, the oolitic limestones are the most important sources for high-brightness limestones.

Oolitic limestones comprise about 20 percent of the Paoli and the Ste. Genevieve along the outcrop belt of southern Indiana (4). They are found as beds of irregular distribution from the upper part of the Paoli to the lower part of the Ste. Genevieve. In an area near Orleans, Orange County, an oolite body was mapped and found to be about 2 miles wide and 4 miles long; its greatest thickness was about 25 feet. The geometry of oolitic limestones is generally lenticular, and where the oolitic facies becomes thinner, it is generally replaced by limestones of less purity In places the oolitic beds are stacked one upon another.

The oolitic limestones consist of fine- to medium-grained ooids that have been cemented with sparry calcite. In thicker beds, say those greater than 8 feet thick, the grains in the upper and lower parts are generally more tightly cemented than are those in the middle. The purity of the oolitic limestones is high, averaging about 98 percent $CaCO_3$ and 1 percent $MgCO_3$.

The distribution of brightness values from a core in Orange County (Figure 8) shows relatively bright limestones for substantial thicknesses. High brightness values are especiall prevalent in the oolitic limestones between 75 and 100 feet. The whiteness of oolitic limestones can be observed in many exposures, but expecially in fresh quarry faces.

The Ste. Genevieve Limestone in Harrison County has several limestones with high brightness (Figure 9) that are not necessarily related to oolites.

Chemical Considerations

We found that brightness was only poorly, if at all, correlated with calcium carbonate (Figure 10A) or iron oxide content (Figure 10B). These figures show only data from the Camden reef, but our plots of other samples show the same trend. The lack of correlation probably indicates that impurities other than iron oxides cause the poor brightness characteristics of rocks of the Muscatatuck Group and the Salem Limestone.

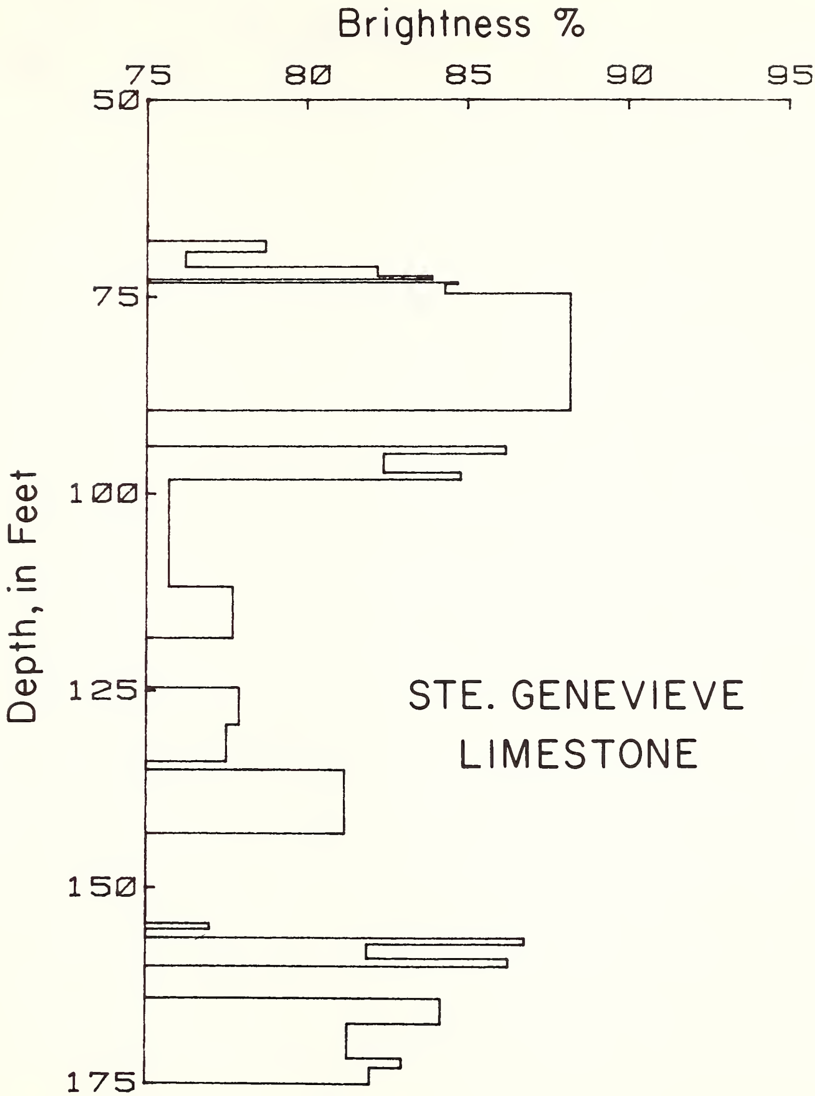

FIGURE 8. *Distribution of brightness values with depth for limestones of the Ste. Genevieve in Orange County.*

Summary

Several limestones, most notably those in the Ste. Genevieve Limestone and the Wabash Formation, have the chemical purity and the brightness values to make them potential raw materials for fillers. Sites in Carroll County in northern Indiana and in Orange County in southern Indiana contain relatively thick sections of suitable limestone and are well located to offer attractive targets for develop-

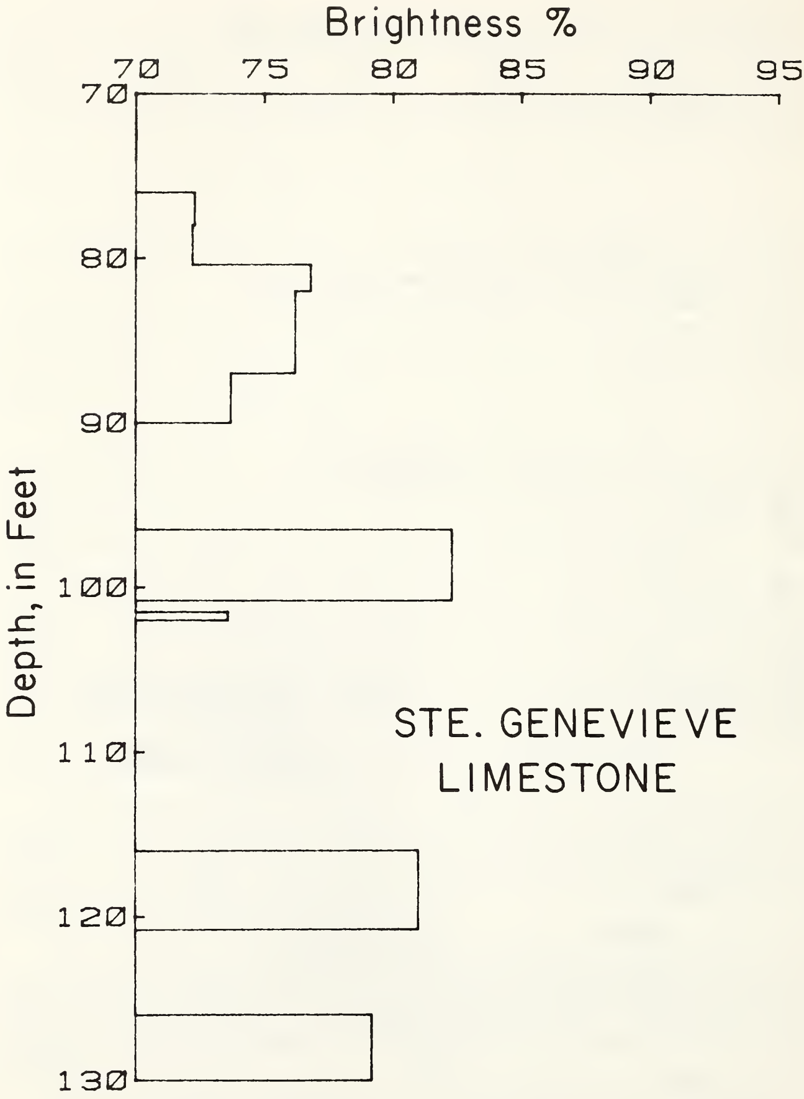

FIGURE 9. *Distribution of brightness values with depth for limestones of the Ste. Genevieve in Harrison County.*

ment. A filler-producing company recently announced that it intended to develop a large white limestone deposit at Camden in northern Indiana. This announcement may indicate that production of filler materials in Indiana is not far in the future.

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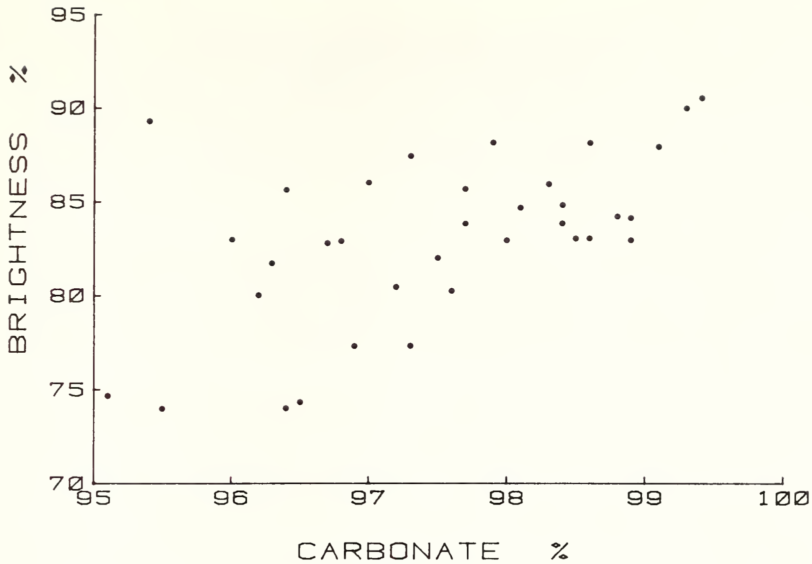

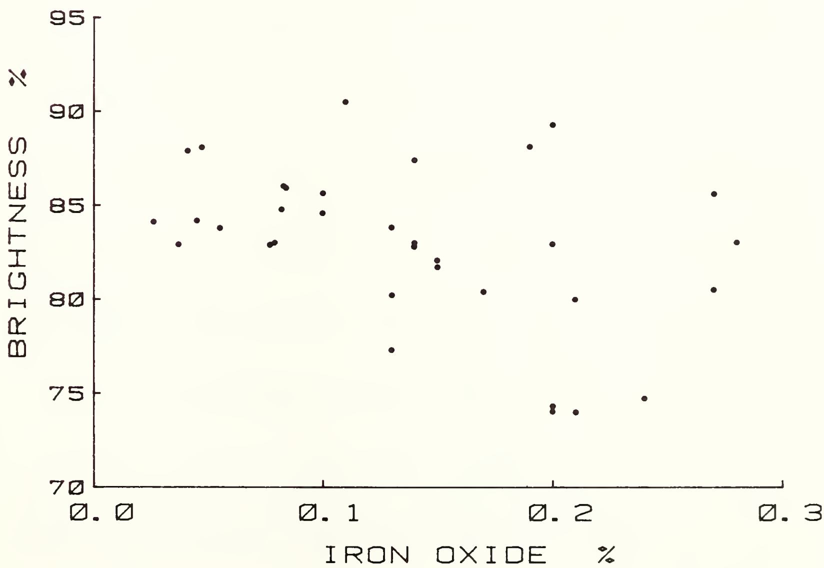

FIGURE 10. *Scatter diagrams showing distribution of brightness values with percentage of calcium carbonate (A) and iron oxide (B) for limestones in the Camden reef, Carroll County.*

information, and the Pulverized Limestone Association for providing information about test procedures.

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