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Low-Silica and High-Calcium Stone in the Newman Limestone (Mississippian) on Pine Mountain, Harlan County, Southeastern Kentucky

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KENTUCKY GEOLOGICAL SURVEY

Donald C. Haney, State Geologist and Director
UNIVERSITY OF KENTUCKY, LEXINGTON

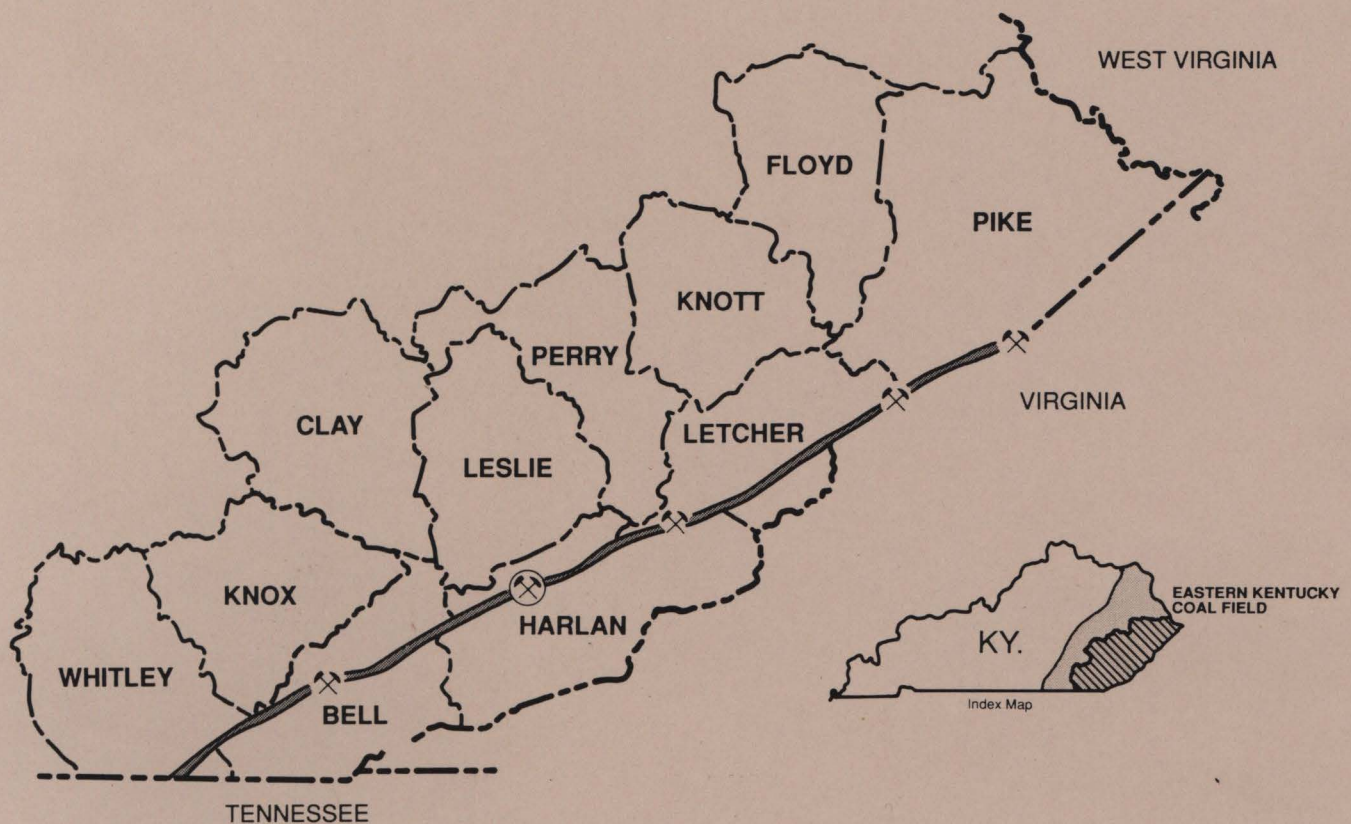
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University of Kentucky, Lexington

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(MISSISSIPPIAN) ON PINE MOUNTAIN,
HARLAN COUNTY, SOUTHEASTERN
KENTUCKY**

Garland R. Dever, Jr.
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LOW-SILICA AND HIGH-CALCIUM STONE IN THE NEWMAN LIMESTONE (MISSISSIPPIAN) ON PINE MOUNTAIN, HARLAN COUNTY, SOUTHEASTERN KENTUCKY

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ABSTRACT

The coal industry of Kentucky is an important market for limestone. Coal producers use limestone as rock dust for explosion abatement in underground coal mines and as a neutralizing agent in surface-mine reclamation and acid-drainage control. Crushed stone is also used for constructing and maintaining haulage roads.

In the Eastern Kentucky Coal Field, the coal-bearing rocks of Pennsylvanian age generally do not contain limestones that are thick enough to quarry or mine economically. But movement on the Pine Mountain overthrust fault has brought the Newman Limestone (Mississippian) to the surface along Pine Mountain in the southeastern part of the coal field.

The Newman on Pine Mountain in Harlan County was sampled at 1-foot intervals to determine its chemical quality and potential for industrial use, particular as low-silica rock dust. The sampled section contains two zones of low-silica stone, 64 and 25 feet thick, averaging 0.82 and 1.01 percent silica (SiO_2), respectively. Intervals of high-calcium limestone are present in the low-silica zones. These deposits are potentially suitable for use as rock dust in underground coal mines and as neutralizing agents in surface-mine reclamation and acid-drainage control.

The intervals of chemically pure stone in Harlan County may be sufficiently thick to produce by selective quarrying or underground mining. Exploitation of the Newman deposits, however, will be complicated by the steep southeastward to southward dip (13 to 42°) of the beds, displacement along small faults within the limestone, and fracturing.

INTRODUCTION

The Eastern Kentucky Coal Field, part of the Appalachian Coal Province, is one of the world's major coal-producing regions (Fig. 1). During the 1988 calendar year, 118.6 million tons of coal were produced from 818 underground mines and 873 surface mines (Stanley, 1989).

With its numerous mines and large production, the coal industry of eastern Kentucky is an important market for limestone. Low-silica limestone is the principal source of rock dust used for explosion abatement in underground coal mines. Construction and maintenance of haulage roads requires limestone aggregate. Agricultural limestone is added to surface-mine soils and spoils to adjust their pH for revegetation. Acid drainage from

mines and refuse piles can be neutralized with high-calcium limestone.

Coal-bearing rocks of Pennsylvanian age in eastern Kentucky principally consist of shale, siltstone, and sandstone, and generally do not contain limestones that are thick enough to quarry or mine economically. However, northwestward movement on the Pine Mountain overthrust fault has brought the Newman Limestone (Mississippian) to the surface in the southeastern part of the coal field where the limestone crops out in a narrow belt along Pine Mountain (Fig. 2).

Five quarries currently are producing construction stone and, to a lesser extent, agricultural stone from the Newman on Pine Mountain, but they furnish only part of the region's requirements. Limestone is brought into

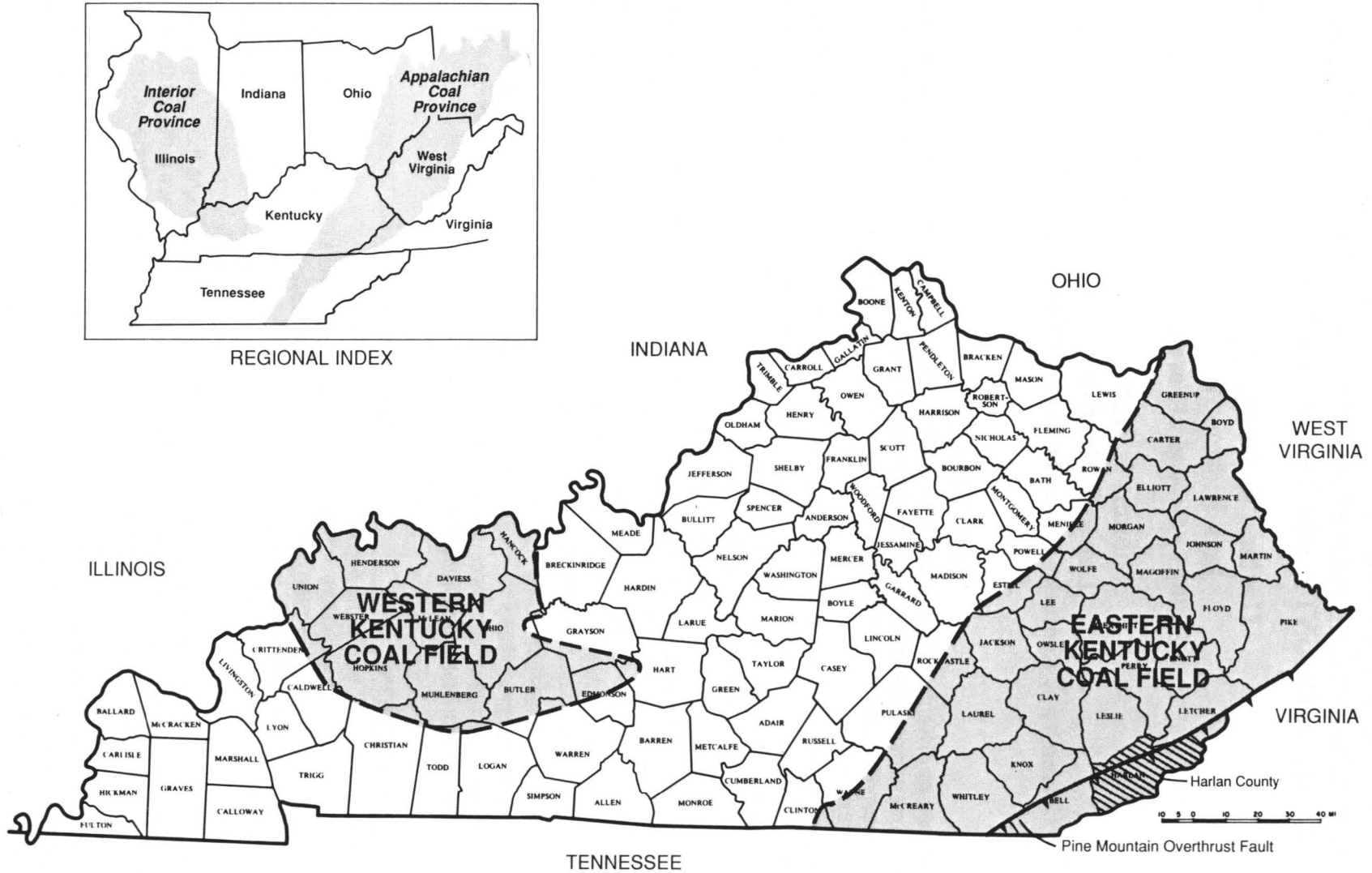


Figure 1. Map of Kentucky showing Eastern and Western Kentucky Coal Fields, and Harlan County study area.

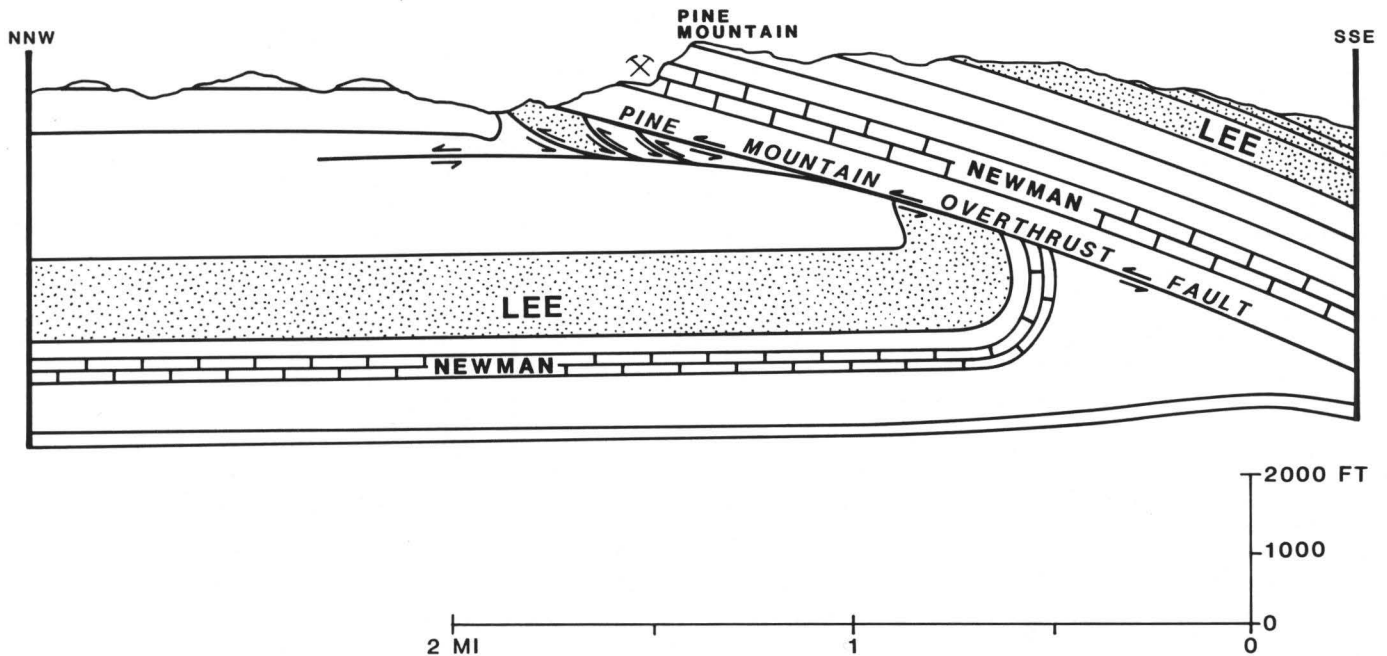


Figure 2. Generalized cross section showing structural setting of Newman Limestone and Harlan Quarry on Pine Mountain. Adapted from Csejtey (1971).

eastern Kentucky from quarries and mines along the western border of the coal field, from central Kentucky, and from operations in adjacent states.

The limestone on Pine Mountain has not been exploited as a source of low-silica rock dust or high-calcium stone for acid-drainage control. Limestone is a low-price bulk commodity, but a major factor in determining its cost is the charge for transportation. The availability of low-silica and high-calcium stone within the coal field should reduce transportation charges and contribute to lower operating costs for coal producers.

The Newman has been sampled at 10 sites along Pine Mountain for major-element analysis to determine the chemical quality of the limestone and to evaluate its potential for industrial use, particularly for the requirements of eastern Kentucky's coal industry (Dever and others, 1985). Samples were taken at 1-foot intervals at each site.

Based on major-element analyses of foot-by-foot samples, the Newman in Harlan County contains two zones of low-silica stone, 64 and 25 feet thick, which are potential sources of rock dust for explosion abatement in underground coal mines (Table 1 and Appendix A). Intervals of high-calcium limestone, potentially suitable for acid-drainage control, are present in the low-silica zones.

Several terms are used in this report for carbonate rocks with chemical characteristics that meet the special requirements of coal producers and other industries. *Low-silica stone* designates carbonate rocks with a total (free and combined) silicon dioxide (SiO_2) content of 4 percent or less, which is the principal chemical specification for materials used as rock dust in underground coal mines (Federal Register Office, 1970). *High-calcium limestone* is composed of 95 percent or more calcium carbonate (CaCO_3). *High-carbonate stone* designates carbonate rocks composed of 95 percent or more total carbonates, calcium carbonate plus magnesium carbonate ($\text{CaCO}_3 + \text{MgCO}_3$).

GEOGRAPHIC AND GEOLOGIC SETTING

The Newman Limestone was sampled in the Nally and Haydon, Inc., Harlan Quarry and adjacent roadcuts along U.S. Highway 421 in northern Harlan County (Fig. 3). The quarry is on the south side of the highway, 5.2 miles north of the intersection of U.S. Highways 421 and 119, and 6.4 miles north of the city of Harlan, the county seat. U.S. Highways 421 and 119 furnish access to the network of State and Federal highways serving the coal-producing areas of southeastern Kentucky. Rail lines into Harlan County, formerly part of the Louisville and Nashville Railroad, are now operated by CSX Transportation. Geologic (Csejtey, 1971) and topographic maps of the Bledsoe Quadrangle, both at a scale of 1:24,000, cover the area of the quarry.

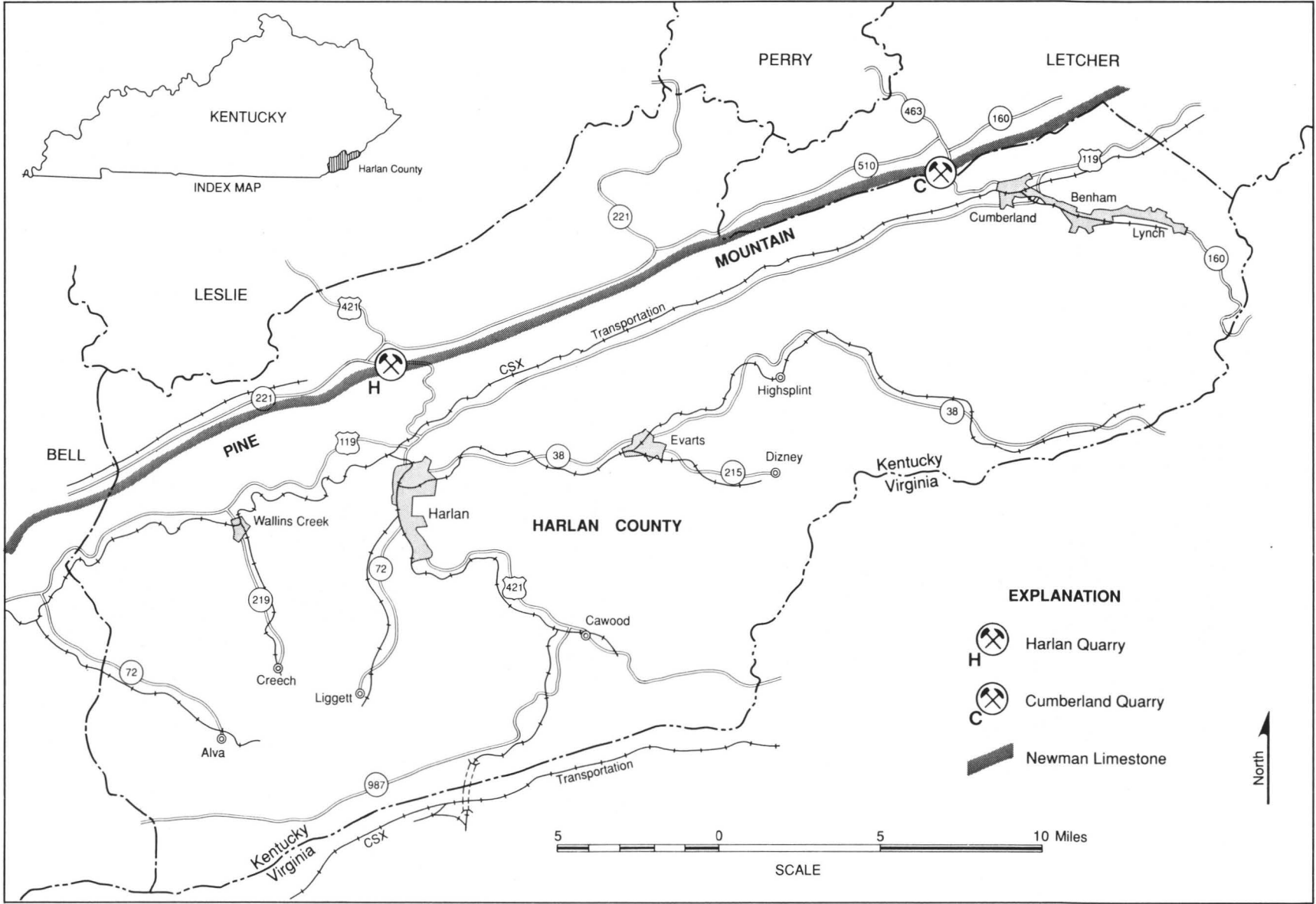


Figure 3. Map of Harlan County showing location of Harlan Quarry, outcrop of Newman Limestone, and transportation network.

Low-Silica and High-Calcium Stone in the Newman Limestone on Pine Mountain

Table 1.—Average Values for Foot-By-Foot Analyses of Principal Intervals of Low-Silica, High-Calcium, and High-Carbonate Stone in Lower Member of Newman Limestone in Harlan County.

Sample Interval (ft.)	Thickness (ft.)	CaCO ₃ + MgCO ₃ (%)	CaCO ₃ (%)	MgCO ₃ (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	K ₂ O (%)	Na ₂ O (%)	S (%)
112-137	25	97.42	96.37	1.05	1.01	0.19	0.10	0.05	0.05	0.01
105-112	7	95.61	91.12	4.49	2.26*	0.54	0.25	0.15	0.08	0.03
68-105	37	98.55	97.33	1.22	0.24	0.09	0.12	0.03	0.05	0.01
41-68	27	97.71	83.21	14.50	1.61	0.16	0.17	0.05	0.03	0.02
COMBINED INTERVALS										
41-105	64	98.19	91.37	6.82	0.82	0.12	0.14	0.04	0.04	0.01
41-137	96	97.80	92.61	5.19	0.97*	0.17	0.14	0.05	0.05	0.01

*Interval includes two 1-foot samples with silica content greater than 4.00 percent (see Appendix A).

The Harlan Quarry is on the northwest face of Pine Mountain, a 125-mile-long, sandstone-capped ridge that extends northeastward from Jellico, Tennessee, to Elkhorn City, Kentucky (Fig. 2). The mountain rises sharply above the Cumberland Plateau to the northwest; relief along the northwest face is as much as 1,360 feet in the vicinity of the quarry.

Pine Mountain lies along the northwest border of the Pine Mountain thrust sheet, and the Pine Mountain overthrust fault underlying the thrust sheet comes to the surface along the northwest side of the mountain (Fig. 2). Northwestward movement of the thrust sheet has brought rocks of Late Devonian, Mississippian, and Early Pennsylvanian age to the surface on Pine Mountain. Elsewhere in the southeastern part of the Eastern Kentucky Coal Field, coal-bearing rocks of Middle Pennsylvanian age are at the surface, both in the Cumberland Plateau, northwest of Pine Mountain, and in the Middlesboro Syncline to the southeast. Strata on Pine Mountain dip steeply southeastward into the Middlesboro Syncline, commonly at angles of 20 to 35° (Froelich, 1973).

NEWMAN LIMESTONE

The Newman Limestone (Mississippian) of southeastern Kentucky is divided into two informal lithologic units, designated as the *lower member* and *upper member*. The lower member of the Newman is principally composed of limestone, with lesser amounts of dolomite and shale, and minor amounts of siltstone and sandstone (Fig. 4). The upper member consists of shale with varied amounts of interbedded limestone, dolomite, siltstone, and sandstone. Economically exploitable deposits of limestone are restricted to the lower member.

A complete section of the Newman is exposed in the Harlan Quarry and adjacent roadcuts (Appendix A). The thickness of the lower member measured 407 feet and

the upper member, 124.5 feet. Lower and upper contacts of the formation are sharp. Limestone at the base of the Newman is underlain by shale of the Grainger Formation. Shale with interbedded sandstone at the top of the upper member is overlain by massive sandstone in the basal part of the Pennington Formation.

To facilitate its description in this report, the lower member of the Newman in the Harlan County section is divided into four lithologic subunits, herein designated, in ascending order, as subunits A, B, C, and D (Fig. 4). The lowest subunit is exposed only in roadcuts west of the quarry. The other subunits are present in the quarry and partly exposed in roadcuts beside and east of the quarry.

Basal *subunit A*, 41 feet thick, mainly consists of dark-colored, cherty calcilutite, capped by silty dolomitic limestone and calcareous dolomite (Appendix A, ledges 1-3). The overlying *subunit B*, 96 feet thick, is composed of light-colored, bioclastic and oolitic calcarenite, with intervals of dolomitic limestone and calcareous dolomite (Appendix A, ledges 4-10). It is the best potential source of low-silica and high-calcium stone.

Subunit C, 15 feet thick, consists of bioclastic calcarenite with interbedded greenish-gray and grayish-red calcilutite and shale in the lower and upper parts of the subunit (Appendix A, ledges 11-13). It is a useful stratigraphic marker in central and northeastern parts of the Newman outcrop belt along Pine Mountain, where the distinctive red and green coloration facilitates its identification (Dever and others, 1985). This subunit was designated as the Taggard Red Member by Wilpolt and Marden (1959). In West Virginia, the Taggard has been placed at the boundary between the Chesterian and Meramecian Series (Wells, 1950) or in the basal part of the Chesterian Series (DeWitt and McGrew, 1979).

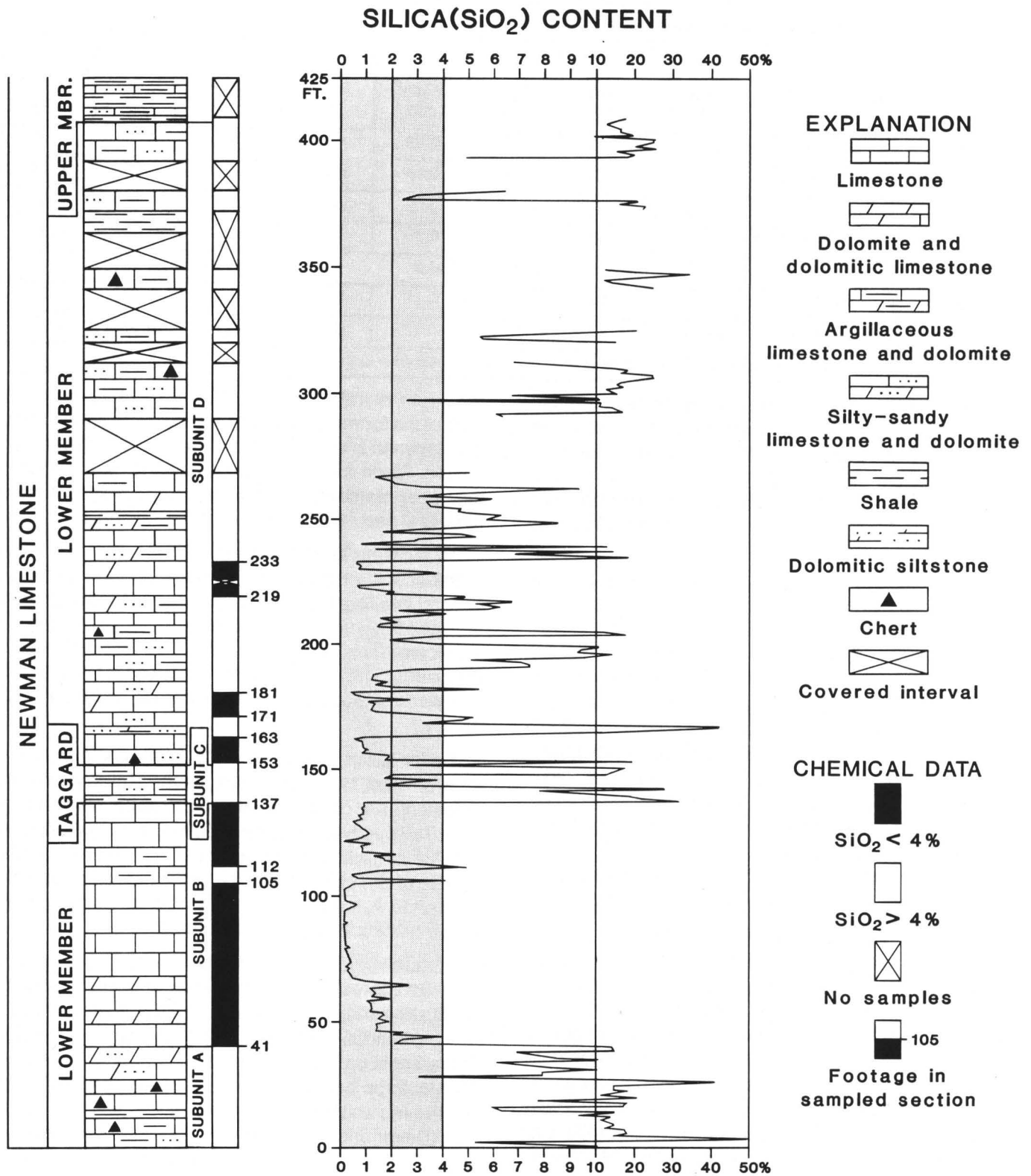


Figure 4. Profile of silica content and generalized lithologies in lower member of Newman Limestone in Harlan Quarry and adjacent roadcuts.

Upper *subunit D*, 255 feet thick, is composed of bioclastic (partly oolitic) calcarenite alternating with argillaceous, silty to sandy limestones (calclutite, calcisiltite, and calcarenite) (Appendix A, ledges 14-33). Shale as much as 8.5 feet thick, dolomitic limestone, calcareous dolomite, and chert also occur in the subunit. The content of detrital quartz and clay in the limestones generally increases upward, reflecting a gradation from the limestone-dominated lower member of the Newman into the shale-dominated upper member.

POTENTIAL INDUSTRIAL USES

Thick zones of low-silica and high-calcium stone are present in a 96-foot interval (subunit B) of the lower member of the Newman Limestone in Harlan County (Fig. 4; Table 1; Appendix A, ledges 4-10). These deposits are potentially suitable for use as rock dust for explosion abatement in underground coal mines and as neutralizing agents in surface-mine reclamation and acid-drainage control. Rock dusting probably will remain the chief defense against coal-dust explosions for the foreseeable future (Sapko and others, 1989).

There is a large market for rock dust in the coal-producing areas northwest and southeast of Pine Mountain. During the 1988 calendar year, 61,514,576 tons of coal were produced by 766 underground mines in 11 southeastern Kentucky counties (Fig. 5) (Stanley, 1989). Rock-dust requirements in the face area of underground coal mines average about 10 pounds of rock dust per ton of mined coal (= 1 ton rock dust per 200 tons coal) (Ralph Perry, Kentucky Department of Mines and Minerals, oral commun., 1983). In terms of 1988 coal-production figures, a minimum of about 307,000 tons of rock dust would be required by underground coal mines in the 11 southeastern Kentucky counties.

Additional quantities of rock dust are needed during mining to maintain the incombustible content of the total amount of dust in the mine, particularly along conveyor-belt haulageways. The incombustible content of the combined coal dust, rock dust, and other dust is mandated to be not less than 65 percent; in the return air-courses, the content is to be not less than 80 percent (Federal Register Office, 1970; Kentucky Department of Mines and Minerals, 1982). A higher incombustible content is required where methane is present in any ventilating current (Federal Register Office, 1970).

For a number of years, out-of-state sources have supplied most, if not all, of the rock dust used in the underground coal mines of southeastern Kentucky. In 1982, two plants in Garrard and Madison Counties of central Kentucky started producing rock dust from the Camp Nelson Limestone (Ordovician) for marketing to

eastern Kentucky mines. The production of rock dust from deposits of low-silica stone on Pine Mountain should contribute to lower operating costs for coal producers in southeastern Kentucky by reducing transportation charges.

Low-Silica Stone for Rock Dust Specifications

Pulverized limestone, dolomite, and other inert materials used as rock dust for explosion abatement in underground coal mines must meet Federal specifications for silica (SiO_2) content. The Federal Coal Mine Health and Safety Act of 1969, Public Law 91-173, states that these materials are not to contain more than a total of 4 percent free and combined silica (Federal Register Office, 1970) (see Appendix B). A low-silica content is specified to reduce the incidence of silicosis through inhalation by miners (Boynton, 1980).

In addition to the silica specification, the 1969 act states that the pulverized limestone or other inert materials used for rock dust are preferred to be light colored, are not to contain more than 5 percent combustible matter, and are to be ground so that 100 percent will pass through a 20-mesh sieve and 70 percent or more will pass through a 200-mesh sieve. It also specifies that "the particles of . . . [rock dust] when wetted and dried will not cohere to form a cake which will not be dispersed into separate particles by a light blast of air" (Federal Register Office, 1970). Low-silica limestone and similar carbonate rocks are considered to produce the best rock dust because their dust has little tendency to cake and its light color aids illumination (U.S. Bureau of Mines, 1960).

Harlan County

Two thick zones of low-silica stone in the Newman of Harlan County are potential sources of rock dust (Fig. 4; Table 1; Appendix A). The lower deposit, 64 feet thick, has an average silica content of 0.82 percent (Appendix A, ledges 4-8); the upper deposit, 25 feet thick, has an average silica content of 1.01 percent (Appendix A, ledge 10).

The two zones are separated by a 7-foot ledge in which two of the seven 1-foot samples have a silica content greater than 4 percent (4.08 and 4.90 percent SiO_2) (Appendix A, ledge 9; Fig. 4). However, with an average silica content of only 0.97 percent, the entire 96-foot interval (subunit B) encompassing the two low-silica zones and the intervening 7-foot ledge may be exploitable as a source of rock dust (Table 1).

The low-silica stone principally consists of very light-gray to light-olive-gray, very fine- to very coarse-grained calcarenite composed of bioclastic, oo-

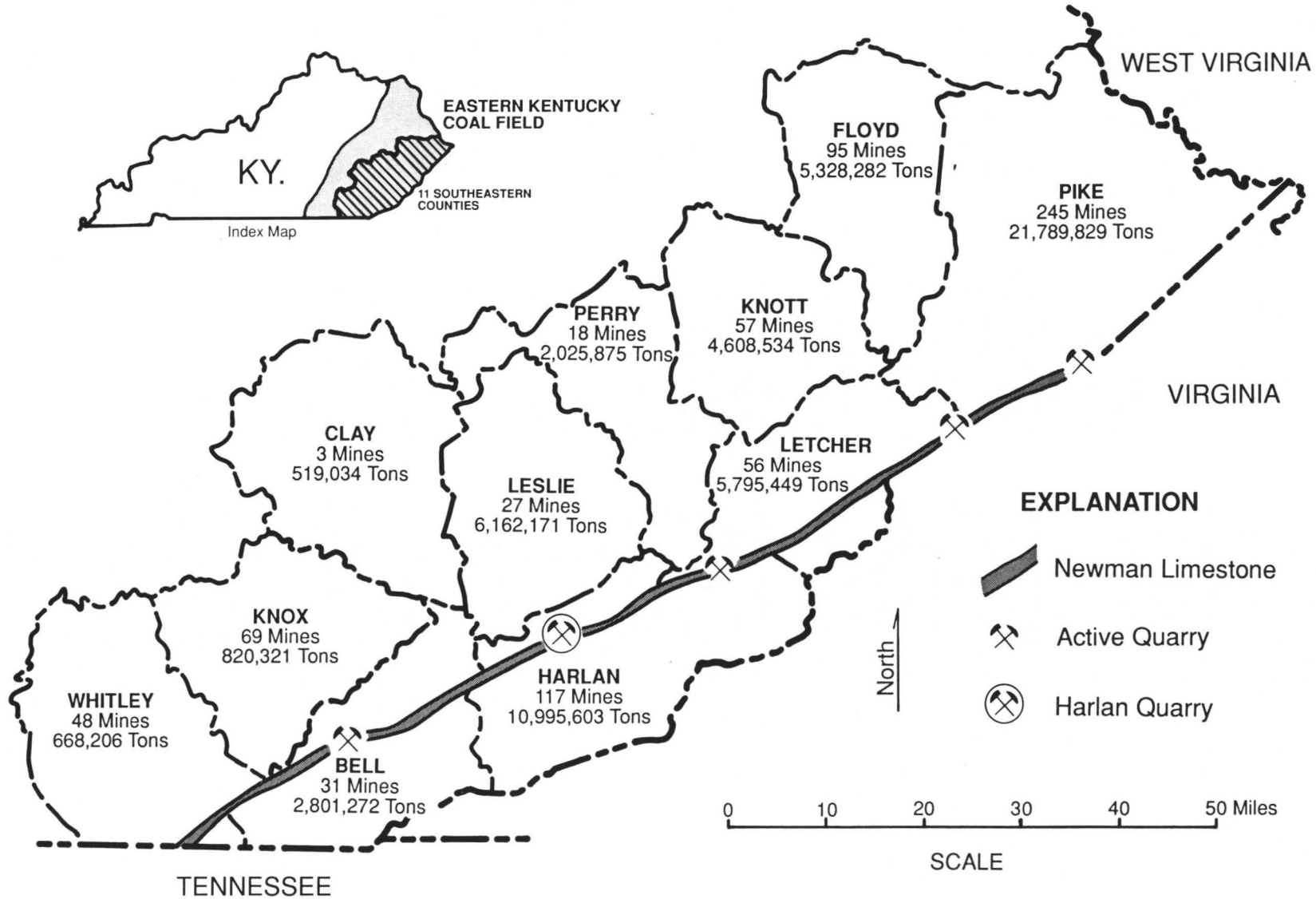


Figure 5. Map indicating potential market for rock dust in southeastern Kentucky. Number of active underground coal mines and their production in 1988 shown by county. Mine and production data from Stanley (1989).

litic, and peloidal grains (Appendix A). Micrite-enveloped bioclastic grains are the dominant constituent. Thin calcilitites occur in the upper deposit. The lower deposit contains zones of very finely crystalline, dolomitic limestone and calcareous dolomite. Dolomitic intervals are very light olive gray to light olive gray and grayish orange to yellowish gray.

The principal source of silica in the 96-foot interval apparently is detrital clay, which forms very thin shales, argillaceous partings, and slightly argillaceous limestones (Appendix A). Small quartz-filled vugs occur rarely in the calcareous dolomite and dolomitic limestone.

Agricultural Stone for Reclamation Specifications

Agricultural stone is applied to surface-mine spoils and replaced topsoil to adjust the pH for revegetation (Barnhisel, 1975; Vogel, 1981; Kentucky Department for Surface Mining Reclamation and Enforcement, 1983). Chemical specifications are in terms of calcium carbonate equivalent (CCE), which is a measure of the stone's acid-neutralizing value.

Carbonate rocks used for agricultural stone must have a minimum CCE value of 80. An arbitrary CCE value of 100 is assigned to pure limestone, composed of 100 percent calcium carbonate (CaCO_3). Pure dolomite, $\text{CaMg}(\text{CO}_3)_2$, which is composed of 54.3 percent CaCO_3 and 45.7 percent MgCO_3 , has a CCE value of 108.6. Pure magnesium carbonate possesses a higher CCE value than pure calcium carbonate because it has a lower molecular weight but the same neutralizing power per molecular unit as calcium carbonate (Boynton, 1980). The factor of MgCO_3 as CaCO_3 equivalent is 1.19 to 1.00.

CCE values can be calculated from the analytical data in Appendix A. Using analyses for the sample from 247-248 feet as an example:

$$\begin{aligned} \text{CaCO}_3(\%) \ 63.76 \times 1.00 &= 63.76 \\ \text{MgCO}_3(\%) \ 23.15 \times 1.19 &= 27.54 \\ \text{CCE value} &= 91.30 \end{aligned}$$

An average CCE value for a quarry ledge or any interval in the sampled section can be calculated after determining the average CaCO_3 and MgCO_3 values:

$$\text{avg. CaCO}_3 + (\text{avg. MgCO}_3 \times 1.19) = \text{avg. CCE}$$

In addition to having a minimum CCE value of 80, stone used for agricultural stone must be ground so that not less than 90 percent will pass through a 10-mesh sieve and not less than 35 percent will pass through a 50-mesh sieve. Neutralization efficiency is a function of both the CCE value and the particle size (Boynton, 1980). The reactive surface area increases as the par-

ticle size decreases, resulting in more rapid reaction. Dolomite, however, reacts more slowly than high-calcium limestone (Boynton, 1980).

Harlan County

Most of the limestone, dolomitic limestone, and calcareous dolomite in the lower member of the Newman Limestone in the Harlan County section meets the chemical specifications for agricultural stone. The high-carbonate limestone and dolomite, and high-calcium limestone in subunit B of the lower member have the highest CCE values (Table 1; Appendix A, ledges 4-8, 10). Intervals that do not meet the specifications for agricultural stone are (1) argillaceous, silty, and sandy limestone in the upper part of subunit D, (2) basal ledge of subunit C, and (3) parts of the cherty limestone in subunit A (Appendix A; Fig. 4).

High-Calcium Limestone for Acid-Drainage Control Specifications

Limestones that are the most effective in neutralizing acid drainage from coal mines and refuse piles have a high calcium carbonate (CaCO_3) content and a low magnesium carbonate (MgCO_3) content (Bituminous Coal Research, Inc., 1970, 1971; Ford, 1974; Hill, 1974; Hill and Wilmoth, 1971). Dolomite and dolomitic limestone, which contain appreciable amounts of magnesium carbonate, react very slowly with acidic waters and are not effective neutralizing agents. The limestone also should have a low percentage of inert constituents, such as silica (SiO_2) and alumina (Al_2O_3) from detrital quartz and clay; their presence means less available alkalinity per ton of stone.

Chemical composition is a critical factor, but the reactivity of pulverized limestone also is related to its effective surface area, which is mainly a function of particle size. The use of smaller size particles results in faster reaction and more effective limestone utilization (Bituminous Coal Research, 1970, 1971; Ford, 1974; Hill and Wilmoth, 1971; Wilmoth, 1974). The recommended maximum particle size is 74 microns (200 mesh) and, if economical, smaller sizes are preferable. Rock dust composed of high-calcium limestone would be suitable for treating acid drainage because limestone used for rock dust must be ground so that 70 percent or more will pass through a 200-mesh sieve.

Harlan County

Intervals of high-calcium limestone, potentially suitable for controlling acid drainage, are present in subunit B of the lower member of the Newman in the Harlan County section. The lower deposit, 37 feet thick, has an average calcium carbonate content of 97.33 percent

(Table 1; Appendix A, ledges 7-8); the upper deposit, 25 feet thick, has an average calcium carbonate content of 96.37 percent (Table 1; Appendix A, ledge 10). The high-calcium limestone coincides with part of the low-silica stone in subunit B (Fig. 4).

The 37-foot and 25-foot deposits of high-calcium limestone are separated by a 7-foot ledge in which four of the seven 1-foot samples have a calcium carbonate content of less than 95 percent (Appendix A, ledge 9). However, with an average calcium carbonate content of 96.35 percent, the entire 69-foot interval encompassing the two high-calcium deposits and the intervening 7-foot ledge may be exploitable as a source of limestone for neutralizing acid drainage (Appendix A, ledges 7-10).

EXPLOITATION

Limestone operations on Pine Mountain commonly have produced stone from steep-walled trenches and pits that have faces as much as 200 feet high. The trenches generally are oriented along the strike of the steeply dipping limestone. Two quarries have benched the limestone rather than working high faces on the sides and ends of trenches and pits. Stone was produced by underground mining in Letcher County, but the mine and adjacent quarry are now closed.

The production of low-silica and high-calcium stone from the Newman in Harlan County will require either selective quarrying or underground mining. The thick, potentially exploitable deposits occur in the lower part of the formation and are overlain by a thick sequence of limestones that contain a relatively high percentage of silica and other noncarbonate constituents (Fig. 4). Several zones of low-silica stone, 10 to 14 feet thick, occur near the middle of the lower member of the Newman, but they probably are too thin to recover economically (Fig. 4).

Both open-pit benching, either on or within a deposit, and underground mining would permit the production of chemically pure stone without contamination from overlying limestones that do not meet the specifications for silica or calcium carbonate content. Underground mining also offers the potential for year-round operation and avoids costs for overburden removal and reclamation (Robertson, 1983).

Production will be complicated by the steep dip of the beds and by faulting within the Newman. In Harlan County, the lower member of the Newman dips to the southeast and south at angles of 13 to 42° (Csejtey, 1970, 1971; Froelich, 1972; Rice, 1975). Dip readings on limestone beds in the Harlan Quarry ranged from 15° S.23°E. to 24° S.5°E. Small-scale thrust faults are relatively common in the Newman and may displace a

deposit of chemically pure stone (Fig. 6a). Repetition of beds by thrust faulting may result in a deposit locally having an apparent thickness greater than its true thickness (Fig. 6b). Both faults and fractures are avenues for the movement of water, soil, and other contaminating materials into a limestone body.

Coring will be required to determine the thickness and lateral extent of a deposit of chemically pure stone and to establish the presence of sufficient reserves to support economic exploitation. Cores also will provide samples for chemical analysis and physical testing.

ACKNOWLEDGMENTS

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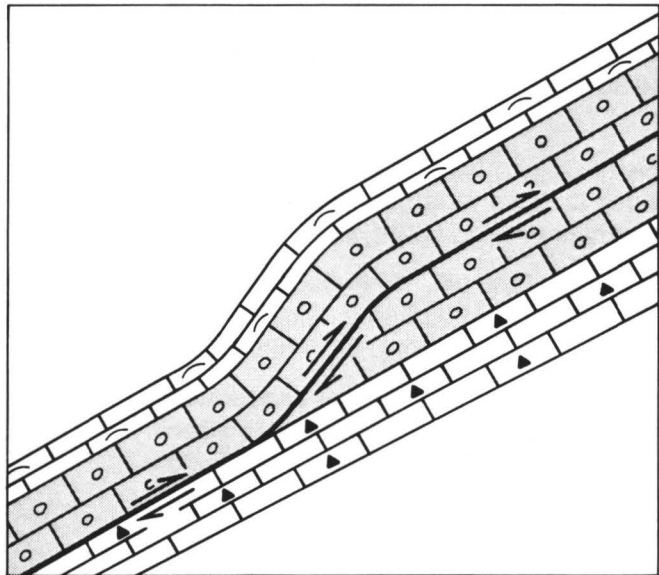
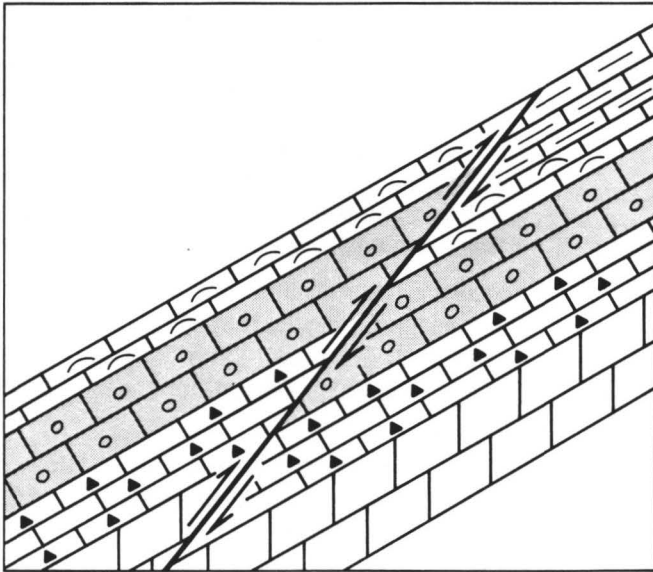


Figure 6. Schematic diagrams showing deposits of chemically pure limestone (shaded) cut by small thrust fault, resulting in offset, or displacement, of deposit (Fig. 6a) and stacking of beds to form anomalously thick deposit (Fig. 6b).

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APPENDIX A:

MAJOR-ELEMENT ANALYSES AND LITHOLOGIC DESCRIPTIONS OF NEWMAN LIMESTONE IN HARLAN QUARRY AND ADJACENT ROADCUTS

County: Harlan	Operator: Nally & Haydon, Inc.
Property Owner: Nally & Haydon, Inc.	
Location: On Pine Mountain, along south side of U.S. Highway 421, 7.2 miles north of Harlan (Harlan County Court-house).	

CHEMICAL ANALYSIS

%	%	%	%	%	%	%	%	%	%
CaCO ₃	MgCO ₃	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	Total	P	S
NO SAMPLES									
NO SAMPLES									
NO SAMPLES									
70.89	2.55	17.03	5.05	2.68	0.73	0.22	99.15	NOT ANALYZED	
71.00	4.21	14.73	4.58	2.97	0.68	0.28	98.45		
77.60	2.12	12.63	3.31	2.03	0.62	0.21	98.52		
70.94	5.53	14.00	4.31	2.48	0.88	0.27	98.41		
66.67	6.06	16.26	4.99	2.70	1.10	0.34	98.12		
66.84	6.32	16.03	4.89	2.40	1.21	0.31	98.00		
66.96	3.72	18.87	5.28	2.26	1.14	0.32	98.55		
81.78	2.92	9.87	2.60	1.42	0.62	0.19	99.40		
51.49	4.24	24.87	5.68	3.11	1.46	0.38	91.23		
55.00	4.66	24.98	5.68	2.98	1.43	0.40	95.13		
61.60	2.11	22.31	5.29	2.67	1.34	0.71	96.03		
66.35	3.15	19.95	5.05	2.06	1.01	0.69	98.26		
59.26	4.29	25.66	5.63	2.91	1.51	0.30	99.56		
72.35	2.88	15.42	4.06	2.29	0.87	0.35	98.22		
62.55	3.29	19.95	5.18	3.23	1.23	0.37	95.80		
67.40	2.90	18.58	4.64	2.24	1.06	0.34	97.16		
88.09	1.94	4.89	4.78	0.58	0.29	0.07	100.64		

Carter Coordinate Location: secs. 5, 6-E-75 (Bledsoe Quadrangle)
Sampled By: Garland R. Dever, Jr., and Jack R. Moody
Analyzed By: Kentucky Center for Energy Research Laboratory
Date Sampled: September–November 1978

DESCRIPTION				
Sample Level (feet)	Ledge No.	Thick-ness (feet)	Lithology	Formation

TOP OF QUARRY FACE

Sandstone of Pennington Formation at top of quarry face and in outcrops on hillside above quarry.

509.5–531.5	38	22	Shale, dark-gray, silty; interbedded with sandstone in thin, wavy beds; scattered brachiopods and carbonized plant remains. Unit forms nearly vertical face.	UPPER MEMBER OF NEWMAN LIMESTONE
454.5–509.5	37	55	Dolomite, medium- to thick-bedded, weathers yellowish orange; interbedded with dark-gray, silty shale and thin beds of fossiliferous limestone. Shale is dominant lithology in middle part of unit.	
409.5–454.5	36	45	Shale, dark-gray, silty, partly fossiliferous, with thin beds of fossiliferous limestone; brachiopods, bryozoans, crinoids, and horn corals.	
408–409.5	35	1.5	Limestone, olive-black to olive-gray, very fine- to fine-grained, silty, argillaceous, shaly; zones of very fine- to very coarse-grained, bioclastic calcarenite; fossiliferous (brachiopods, bryozoans, and crinoids); traces of pyrite; one bed; weathers yellowish orange.	
407–408	34	1	Shale, dark-gray, with few very thin beds of limestone. Limestone, olive-gray to olive-black, very fine- to fine-grained, silty, argillaceous; zones of very fine- to coarse-grained, bioclastic calcarenite, commonly in an argillaceous matrix; fossiliferous (brachiopods, bryozoans, and crinoids); traces of pyrite. Only limestone was sampled for analysis.	

406–407	33	15	Limestone, olive-black, very fine- to fine-grained, silty to sandy, argillaceous; zones of very fine- to very coarse-grained, bioclastic calcarenite, commonly in an argillaceous matrix (few grains silicified); fossiliferous (crinoids, brachiopods, bryozoans, and horn corals); traces of pyrite in interval 393–399 feet; medium- to thick-bedded; very thin-bedded with very thin shales in upper 1/2 foot. Top ledge of main quarry face.	LOWER MEMBER OF NEWMAN LIMESTONE
405–406				
404–405				
403–404				
402–403				
401–402				
400–401				
399–400				
398–399				
397–398				
396–397				
395–396				
394–395				
393–394				
392–393				

CHEMICAL ANALYSIS

% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
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NO SAMPLES

85.09	2.22	6.46	4.32	0.64	0.37	0.11	99.21	NOT ANALYZED
91.94	1.75	3.12	2.73	0.78	0.19	0.10	100.61	
91.37	1.49	2.76	2.01	0.23	0.09	0.10	98.05	
92.09	1.42	2.42	2.04	0.22	0.08	0.08	98.35	
70.99	2.75	21.05	2.23	1.72	0.91	0.20	99.85	
74.73	2.35	15.96	2.70	1.39	0.79	0.17	98.09	
63.22	3.24	22.87	4.97	1.94	1.37	0.27	97.88	
66.89	3.03	22.14	4.24	1.70	1.27	0.25	99.52	

NO SAMPLES

86.51	2.10	8.18	1.72	0.71	0.48	0.16	99.86
NO SAMPLES							
80.22	2.73	12.68	2.29	0.89	0.57	0.22	99.60
72.57	2.42	20.33	1.91	0.95	0.48	0.21	98.87
59.93	2.52	34.43	1.34	0.79	0.36	0.18	99.55
70.44	2.24	22.09	2.01	0.94	0.46	0.23	98.41
81.32	2.68	12.08	2.22	0.91	0.44	0.21	99.86
77.33	2.89	14.28	2.17	0.93	0.31	0.21	98.12
70.70	2.84	21.64	2.04	1.05	0.53	0.30	99.10
66.27	2.84	24.84	2.09	1.03	0.82	0.21	98.10

NO SAMPLES

69.16	2.92	20.31	3.91	1.95	1.23	0.21	99.69
87.12	1.99	8.02	1.71	0.92	0.12	0.14	100.02
90.04	2.04	5.45	1.28	0.98	0.32	0.12	100.23
90.22	1.87	5.54	1.39	0.80	0.32	0.11	100.25
77.42	2.11	15.51	2.77	1.50	0.78	0.21	100.30

NO SAMPLES

DESCRIPTION				
Sample Level (feet)	Ledge No.	Thickness (feet)	Lithology	Formation
380.5-392	12	11.5	Covered on upper bench; inaccessible in quarry face.	
379.5-380.5 378.5-379.5 377.5-378.5 376.5-377.5 375.5-376.5 374.5-375.5 373.5-374.5 372.5-373.5	31	8	Limestone, olive-gray to medium-light-olive-gray, fine- to very coarse-grained, bioclastic (in part micrite-enveloped grains), peloidal, partly oolitic, in part silty to sandy, in a micrograined to argillaceous matrix; in part very fine-grained limestone, silty to sandy, argillaceous, partly shaly, with thin zones of bioclastic calcarenite; sparsely fossiliferous (crinoids and brachiopods); few stylolites; thin- to medium-bedded.	
364-372.5	30	8.5	Shale, greenish-gray and grayish-red, indurated, calcareous, silty to sandy; scattered bioclastic grains in upper part.	
363-364 349-363 348-349 347-348 346-347 345-346 344-345 343-344 342-343 341-342	29	23	Limestone, olive-gray, very fine-grained to very finely crystalline, slightly argillaceous, with bioclastic grains (in part silicified); zones of very fine- to very coarse-grained, bioclastic calcarenite (grains in part silicified); in part oolitic in upper foot; irregular areas of dark-greenish-gray, argillaceous limestone in upper foot; fossiliferous (crinoids, bryozoans, brachiopods, horn corals, and echinoids; in part silicified); nodules and thin lenses of chert (with relict calcarenitic texture) common in lower part; thick-bedded, with few argillaceous partings; thin-bedded appearance in weathered exposures. Interval 349-363 feet covered on upper bench.	
325-341	28	16	Covered on upper bench; inaccessible in quarry face.	
324-325 323-324 322-323 321-322 320-321	27	5	Limestone, medium-light-olive-gray to light-olive-gray, fine- to coarse-grained, bioclastic (mainly micrite-enveloped grains; few grains silicified), oolitic, sparsely peloidal; zones and irregular areas of very dusky-red-purple and greenish-gray, silty, argillaceous limestone and calcareous shale (dominant lithology in basal foot and upper foot); in part fossiliferous (crinoids and brachiopods); medium-bedded.	
312-320	26	8	Covered on upper bench; inaccessible in quarry face.	

LOWER MEMBER OF NEWMAN LIMESTONE

CHEMICAL ANALYSIS									
% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
87.66	2.10	6.76	1.48	0.67	0.31	0.15	99.13	NOT ANALYZED	
85.26	2.25	9.30	1.92	0.83	0.41	0.19	100.16		
78.26	2.57	15.15	2.21	0.98	0.74	0.23	100.14		
76.97	2.53	17.75	2.12	0.92	0.15	0.20	100.64		
76.11	2.68	16.16	2.49	1.30	0.71	0.28	99.73		
68.15	2.25	24.20	1.79	0.93	0.49	0.20	98.01		
67.35	2.26	24.62	1.93	1.21	0.50	0.22	98.09		
73.79	2.65	18.15	2.84	1.50	0.49	0.31	99.73		
78.09	2.28	16.16	2.19	1.09	0.47	0.23	100.51		
76.68	2.48	15.94	2.51	1.35	0.65	0.26	99.87		
76.15	2.36	16.94	2.50	1.51	0.61	0.27	100.34		
79.76	2.13	12.85	2.13	1.17	0.57	0.22	98.83		
77.86	2.40	15.87	1.07	1.13	0.60	0.25	99.18		
88.70	1.72	6.70	2.33	0.73	0.24	0.17	100.59		
82.23	2.50	11.10	2.03	1.16	0.43	0.16	99.61		
92.14	1.49	2.55	1.64	0.39	0.15	0.11	98.47		
79.38	2.43	11.55	3.33	0.76	0.45	0.22	98.12		
82.49	1.74	11.05	1.72	0.78	0.42	0.19	98.39		
79.84	1.64	13.90	1.77	1.29	0.41	0.19	99.04		
74.12	2.52	16.39	2.92	1.59	0.61	0.28	98.43		
88.50	1.56	6.18	1.06	0.44	0.23	0.13	98.10		
89.60	1.85	6.34	1.30	0.42	0.29	0.16	99.96		
NO SAMPLES									
80.88	9.61	5.08	1.52	0.48	0.30	0.13	98.00		
94.92	1.31	2.62	0.63	0.09	0.19	0.09	99.85		
95.86	1.10	1.41	0.27	0.02	0.07	0.07	98.80		
94.61	1.36	2.05	0.44	0.07	0.09	0.08	98.70		
93.12	2.40	2.16	0.43	0.09	0.09	0.08	98.37		
89.72	5.23	3.18	0.64	0.15	0.19	0.10	99.21		
78.60	7.41	9.11	1.71	0.64	0.36	0.20	98.03		
87.29	1.96	7.85	1.63	0.61	0.34	0.16	99.84		
87.91	5.44	4.15	0.83	0.28	0.15	0.09	98.85		
89.91	4.69	3.10	0.65	0.19	0.13	0.11	98.78		
86.75	4.60	5.88	1.28	0.38	0.25	0.14	99.28		
85.87	5.16	5.27	1.20	0.50	0.23	0.14	98.37		
89.07	4.09	3.43	0.75	0.18	0.15	0.06	97.73		
91.08	3.75	3.52	0.85	0.40	0.16	0.10	99.86		
86.59	5.27	4.69	0.92	0.27	0.21	0.07	98.02		
87.84	4.13	4.60	0.90	0.28	0.20	0.08	98.03		
87.72	3.73	5.04	1.75	0.47	0.25	0.08	99.04		
86.16	3.40	6.34	2.18	0.47	0.34	0.13	99.02		

DESCRIPTION

Sample Level (feet)	Ledge No.	Thick-ness (feet)	Lithology	Formation
311-312				
310-311				
309-310				
308-309				
307-308				
306-307				
305-306				
304-305				
303-304				
302-303				
301-302				
300-300	25	22	Limestone, olive-black to olive-gray, greenish-black to greenish-gray, and brownish-gray, micrograined to microcrystalline, argillaceous and silty, with varied amounts of bioclastic grains (in part silicified); beds and zones, mainly in lower 14 feet, of olive-black to light-olive-gray, and greenish-black, very fine- to very coarse-grained, bioclastic calcarenite, mainly in a micrograined to argillaceous matrix; fossiliferous (crinoids, brachiopods, and horn corals; in part silicified); nodular chert in intervals 305-307 and 308-309 feet; trace of pyrite in intervals 290-291 and 295-296 feet; medium- to thick-bedded.	
299-300				
298-299				
297-298				
296-297				
295-296				
294-295				
293-294				
292-293				
291-292				
290-291				
268-290	24	22	Covered on hillside; inaccessible in quarry face.	
267-268				
266-267				
265-266				
264-265	23	6	Limestone, medium-light-olive-gray, micrograined, with abundant bioclastic grains; in part very fine- to coarse-grained, bioclastic and peloidal calcarenite; sparsely fossiliferous (crinoids and brachiopods); breccia zone at top of ledge consisting of olive-gray, brecciated micrograined limestone (scattered birdseyes of crystalline calcite) in a matrix of greenish-gray shale and dusky-yellow, very finely crystalline dolomite; mineral-lined vugs locally in weathered exposures; thick-bedded.	
263-264				
262-263				
261-262				
260-261				
259-260				
258-259				
257-258				
256-257				
255-256	22	12	Limestone, medium-light-olive-gray, micrograined, in part slightly argillaceous, with varied amounts of bioclastic grains; very thin zones of yellowish-gray, very finely crystalline dolomite; fossiliferous (crinoids, bryozoans, brachiopods, and gastropods) in lower 8 feet; few scattered crystals of reddish quartz in intervals 254-255, 259-260, and 261-262 feet; few stylolites; thin- to medium-bedded, with slightly irregular bedding; thin shales in basal foot.	
254-255				
253-254				
252-253				
251-252				
250-251				

LOWER MEMBER OF NEWMAN LIMESTONE

CHEMICAL ANALYSIS									
% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
56.62	33.95	5.71	1.44	0.76	0.17	0.10	98.75	NOT ANALYZED	
52.90	34.37	8.50	1.99	0.84	0.23	0.07	98.70		
63.76	23.15	7.96	2.40	0.71	0.38	0.13	98.49		
76.43	15.05	5.41	1.19	0.35	0.37	0.11	98.91		
75.77	17.56	3.31	0.76	0.29	0.19	0.12	98.00		
93.74	3.28	1.59	0.32	0.05	0.12	0.05	99.15		
85.96	5.37	4.78	1.29	0.29	0.28	0.10	98.07		
81.01	9.83	5.43	1.33	0.39	0.30	0.11	98.40		
93.39	1.91	3.11	0.70	0.28	0.20	0.18	99.77		
93.56	2.82	2.86	0.60	0.24	0.14	0.11	100.33		
92.49	4.74	0.87	0.23	0.24	0.05	0.08	98.70		
76.63	5.23	13.21	2.70	1.02	0.71	0.25	99.75		
94.37	1.71	1.44	0.40	0.17	0.07	0.07	98.23		
68.22	12.37	14.00	2.30	1.13	0.53	0.16	98.71		
80.12	9.74	6.97	1.53	0.52	0.36	0.15	99.39		
76.86	1.07	18.72	1.89	1.27	0.50	0.28	100.59		
78.95	12.18	6.15	1.53	0.54	0.33	0.15	99.83		
96.42	1.22	0.63	0.15	0.24	0.05	0.07	98.78		
97.39	1.17	0.59	0.20	0.19	0.05	0.12	99.71		
97.59	1.11	0.79	0.15	0.19	0.04	0.06	99.93		
88.09	9.26	0.73	0.13	0.50	0.04	0.07	98.82		
79.84	14.33	3.46	1.20	1.49	0.24	0.13	100.69		
76.77	17.10	3.83	1.10	0.50	0.23	0.15	99.68		
93.04	3.97	1.40	0.37	0.20	0.10	0.08	99.16		
NO SAMPLES									
93.25	1.97	1.86	0.52	0.29	0.14	0.07	98.10		
98.21	1.23	0.62	0.10	0.20	0.04	0.06	100.46		
95.38	4.01	0.70	0.14	0.30	0.10	0.09	100.72		
93.89	1.68	2.15	0.31	0.18	0.09	0.09	98.39		
93.10	2.96	1.77	0.55	0.21	0.14	0.10	98.83		
83.59	9.47	4.99	1.10	0.40	0.25	0.17	99.97		
82.10	11.29	4.05	0.93	0.36	0.21	0.10	99.04		
82.34	6.72	6.69	1.42	0.40	0.30	0.13	98.00		
87.33	4.26	5.35	0.97	0.30	0.21	0.12	98.54		
84.28	6.79	6.42	1.37	0.38	0.29	0.10	99.63		
87.39	4.40	5.67	1.33	0.32	0.34	0.16	99.61		
92.60	2.89	2.32	0.33	0.07	0.07	0.10	98.38		
89.29	3.85	4.15	0.43	0.14	0.08	0.07	98.01		
88.59	7.08	3.17	0.50	0.17	0.09	0.07	99.67		
93.95	2.49	1.54	0.26	0.04	0.04	0.04	98.36		
88.39	6.92	2.36	0.40	0.12	0.07	0.05	98.31		
94.79	1.86	1.55	0.21	0.02	0.04	0.06	98.53		
93.97	2.06	1.46	0.33	0.08	0.05	0.06	98.01		
90.81	3.04	3.45	0.49	0.14	0.08	0.10	98.11		
61.72	21.23	12.95	1.22	0.56	0.13	0.19	98.00		
61.53	17.09	17.49	1.42	0.44	0.17	0.28	98.42		
91.15	2.15	3.88	1.36	0.07	0.05	0.03	98.69		

DESCRIPTION				
Sample Level (feet)	Ledge No.	Thick-ness (feet)	Lithology	Formation
249-250	21	14	Limestone, medium-light-olive-gray to light-olive-gray and greenish-gray, micrograined to very finely crystalline, in part dolomitic, in part silty and argillaceous, with varied amounts of bioclastic and peloidal grains; interbedded with light-olive-gray, fine to coarse-grained calcarenite, bioclastic (in part micrite-enveloped grains), peloidal, and slightly oolitic; medium-light-olive-gray, very finely crystalline dolomite, silty and slightly argillaceous, in upper 2 feet; sparsely fossiliferous (crinoids, bryozoans, and brachiopods); few stylolites; medium- to thick-bedded; nodular and irregular bedding in interval 241.5 to 244 feet.	
248-249				
247-248				
246-247				
245-246				
244-245				
243-244				
242-243				
241-242				
240-241				
239-240				
238-239	20	3	Limestone, olive-gray, very fine- to very coarse-grained, bioclastic (some micrite-enveloped grains), peloidal, mainly in a microcrystalline to very finely crystalline, dolomitic matrix; slightly argillaceous and silty; light-gray, silty, earthy limestone in interval 234-235 feet; thin- to medium-bedded, with very thin shales; thin shale at top laterally thickens to 10 inches.	
237-238				
236-237				
235-236				
234-235				
233-234				
232-233				
231-232				
230-231				
229-230				
228-229				
227-228	19	31	Limestone, medium-light-olive-gray to light-olive-gray, very fine- to very coarse-grained, bioclastic (commonly micrite-enveloped grains), peloidal, oolitic; interbedded with olive-gray to medium-light-olive-gray, micrograined to very finely crystalline limestone, in part dolomitic, slightly argillaceous and silty, with varied amounts of bioclastic grains; erosional clasts of micrograined limestone and diagenetic micritic crusts in peloidal calcarenite at base of ledge; fossiliferous (crinoids, brachiopods, bryozoans, horn corals, and echinoids; locally silicified); small bodies of dark-brownish-gray chert locally in interval 202-203 feet; thin stringers and small bodies of crystalline quartz in interval 203-205 feet; few scattered traces of pyrite; stylolites; thin- to thick-bedded; few argillaceous partings and very thin shales in interval 209-219 feet. Erosional contact with underlying ledge.	
226-227				
224-226				
223-224				
222-223				
221-222				
220-221				
219-220				
218-219				
217-218				
216-217				
215-216				
214-215				
213-214				
212-213				
211-212				
210-211				
209-210				
208-209				
207-208				
206-207				
205-206				
204-205				
203-204				
202-203				

LOWER MEMBER OF NEWMAN LIMESTONE

CHEMICAL ANALYSIS									
% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
94.64	2.16	2.19	0.53	0.05	0.05	0.03	99.65	NOT ANALYZED	
95.68	2.15	1.92	0.36	0.05	0.05	0.04	100.25		
91.81	2.69	3.91	0.68	0.16	0.09	0.05	99.39		
81.52	4.08	10.11	1.52	0.46	0.24	0.08	98.01		
83.07	4.22	9.45	1.48	0.48	0.23	0.08	99.01		
83.94	4.14	9.26	1.56	0.50	0.27	0.08	99.75		
78.05	5.68	13.82	1.85	0.93	0.41	0.08	100.82		
84.77	4.12	9.46	1.44	0.62	0.25	0.06	100.72		
89.03	2.37	5.19	0.82	0.52	0.13	0.06	98.12		
87.46	2.72	7.04	1.14	0.43	0.16	0.10	99.05		
86.36	2.80	7.41	1.02	0.35	0.15	0.12	98.21		
86.93	3.24	7.46	1.08	0.41	0.18	0.09	99.39		
92.38	2.89	2.88	0.37	0.15	0.05	0.06	98.78	NA	0.03
94.09	1.82	1.77	0.29	0.07	0.02	0.02	98.08		0.03
93.23	2.98	1.27	0.35	0.16	0.04	0.03	98.06		0.03
94.01	3.43	1.25	0.31	0.16	0.04	0.04	99.24		0.03
95.17	3.07	1.20	0.21	0.11	0.03	0.04	99.83		0.03
89.47	6.90	1.87	0.56	0.24	0.10	0.04	99.18		0.02
92.93	3.39	1.33	0.19	0.12	0.03	0.03	98.02		0.03
91.16	6.28	2.24	0.37	0.23	0.07	0.03	100.38		0.04
79.12	14.70	5.40	0.98	0.26	0.09	0.07	100.62		0.03
96.19	2.89	0.44	0.08	0.09	0.02	0.07	99.78		0.03
92.33	5.77	0.53	0.01	0.10	0.02	0.07	98.83		0.03
95.49	3.39	0.82	0.31	0.07	0.02	0.07	100.17		0.02
93.17	4.10	2.76	0.15	0.08	0.02	0.07	100.35		0.02
87.08	10.00	1.01	0.15	0.13	0.04	0.10	98.51		0.02
89.34	8.34	1.41	0.10	0.12	0.03	0.08	99.42		0.02
86.32	11.09	1.28	0.11	0.12	0.03	0.07	99.02		0.02
91.07	7.19	1.24	0.10	0.11	0.03	0.08	99.82		0.03
91.85	6.05	1.40	0.10	0.11	0.02	0.07	99.60		0.02
83.62	12.65	3.05	0.24	0.16	0.04	0.07	99.83		0.03
90.31	2.07	5.22	0.62	0.30	0.10	0.08	98.70		0.03
90.56	2.34	4.81	0.59	0.26	0.13	0.07	98.76		0.03
91.94	3.67	3.20	0.33	0.18	0.08	0.05	99.45		0.03
75.77	6.72	12.56	2.11	0.86	0.44	0.14	98.60		0.02
32.78	12.89	42.13	5.78	2.70	1.90	0.39	98.28	NOT ANALYZED	
82.15	4.80	10.91	1.29	0.51	0.21	0.09	99.96		

NA = Not Analyzed

DESCRIPTION				
Sample Level (feet)	Ledge No.	Thickness (feet)	Lithology	Formation
201-202				
200-201				
199-200				
198-199				
197-198				
196-197	18	12		
195-196				
194-195				
193-194				
192-193				
191-192				
190-191				
			Limestone, olive-gray, micrograined to very fine-grained, silty, slightly argillaceous, with varied amounts of bioclastic grains; in part very fine- to very coarse-grained calcarenite, bioclastic (few micrite-enveloped grains), mainly in a micrograined to microcrystalline matrix; fossiliferous (crinoids, brachiopods, bryozoans, and horn corals; in part silicified); traces of diagenetic micritic stringers (brownish-black and light-brownish-gray) in upper foot; traces of pyrite in intervals 193-194 and 195-200 feet; thin to thick, planar beds in lower part; nodular to indistinct bedding in upper part; argillaceous partings and very thin shales. Erosional contact with overlying ledge.	
189-190				
188-189				
187-188				
186-187				
185-186				
184-185	17	10		
183-184				
182-183				
181-182				
180-181				
			Limestone, medium-light-olive-gray to olive-gray, very fine- to very coarse-grained, bioclastic (in part micrite-enveloped grains), peloidal, oolitic, commonly in a micrograined to very finely crystalline matrix; fossiliferous (crinoids, brachiopods, and horn corals; in part silicified); thin bands of yellowish-gray to light-olive-gray, very finely crystalline dolomite in interval 181-182 feet; few scattered quartz grains in interval 182-186 feet; few stylolites; thin- to thick-bedded; crossbedded.	
179-180				
178-179				
177-178				
176-177				
175-176				
174-175				
173-174				
172-173	16	13		
171-172				
170-171				
169-170				
168-169				
167-168				
			Limestone, light-olive-gray to olive-gray, very fine- to very coarse-grained, bioclastic (in part micrite-enveloped grains), peloidal, oolitic; locally grades into very finely crystalline, dolomitic limestone; zones of microcrystalline to micrograined limestone (in part silty; in part dolomitic) in lower 5 feet; locally fossiliferous (crinoids, bryozoans, and brachiopods); quartz-lined and calcite-filled vugs in intervals 171-172 and 179-180 feet; traces of pyrite in lower 3 feet; few stylolites; massive.	
166-167				
164.5-166	15	2.5		
			Limestone, olive-gray, very fine- to very coarse-grained, peloidal, bioclastic (in part micrite-enveloped grains), oolitic, silty, with scattered clasts of micrograined and calcarenitic limestone; irregular areas of greenish-gray, silty, argillaceous, microcrystalline limestone; olive-black, argillaceous, dolomitic siltstone, with abundant peloidal grains in upper foot; traces of pyrite; medium-bedded, with thin shales.	

LOWER MEMBER OF NEWMAN LIMESTONE

CHEMICAL ANALYSIS									
% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
87.85	3.00	6.76	0.58	0.24	0.09	0.03	98.55	NA	0.02
95.20	1.72	0.97	0.12	0.06	0.02	0.03	98.12		0.02
96.03	1.47	0.50	0.24	0.07	0.02	0.02	98.35		0.03
95.81	1.52	0.84	0.00	0.05	0.02	0.03	98.27		0.03
95.28	1.67	0.86	0.08	0.05	0.02	0.04	98.00		0.02
95.27	1.72	0.85	0.08	0.07	0.02	0.03	98.04		0.03
95.21	1.50	1.02	0.06	0.17	0.02	0.03	98.01		0.02
95.81	1.40	0.87	0.07	0.07	0.02	0.02	98.26		0.02
96.04	1.43	1.82	0.06	0.08	0.02	0.04	99.49		0.02
95.42	1.42	1.84	0.13	0.08	0.02	0.03	98.94		0.02
94.71	1.32	1.75	0.10	0.08	0.02	0.02	98.00		0.02
70.07	4.44	19.12	3.37	1.44	0.03	0.30	98.77		0.03
93.69	1.46	2.69	0.31	0.14	0.04	0.02	98.35	NOT ANALYZED	
75.33	3.04	17.31	2.13	0.85	0.43	0.29	99.38		
77.36	3.19	15.82	2.30	0.89	0.45	0.27	100.28		
79.64	3.14	13.11	2.01	0.53	0.45	0.19	99.07		
94.63	1.85	2.03	0.26	0.12	0.05	0.02	98.96		
94.76	1.63	1.69	0.20	0.07	0.02	0.02	98.39		
92.99	1.82	3.85	0.15	0.15	0.05	0.04	99.05		
94.21	1.46	2.49	0.10	0.06	0.03	0.02	98.37		
94.68	1.33	1.71	0.17	0.07	0.08	0.02	98.06		
60.58	4.31	27.25	3.59	1.91	1.32	0.40	99.36		
84.66	2.55	7.79	1.72	0.68	0.48	0.12	98.00		
NO SAMPLE									
74.48	2.39	18.73	2.87	1.15	0.89	0.29	100.80		
67.32	2.96	22.37	3.79	1.45	1.05	0.38	99.32		
52.27	4.32	31.75	5.11	2.40	1.76	0.44	98.05		
95.94	1.18	0.97	0.07	0.08	0.04	0.01	98.29	NA	0.02
95.84	1.12	0.96	0.11	0.09	0.04	0.02	98.18		0.02
96.12	1.07	0.86	0.06	0.10	0.06	0.02	98.29		0.01
95.65	1.04	0.92	0.19	0.10	0.06	0.04	98.00		0.02
96.29	1.00	0.88	0.10	0.10	0.06	0.05	98.48		0.01
95.91	1.06	0.69	0.14	0.09	0.04	0.08	98.01		0.01
96.22	1.05	0.84	0.16	0.09	0.04	0.03	98.43		0.01
97.60	1.01	0.50	0.14	0.09	0.05	0.05	99.44		0.01
97.06	1.14	0.53	0.14	0.10	0.06	0.03	99.06		0.01
NO SAMPLE									
96.80	1.19	0.87	0.20	0.12	0.06	0.04	99.28		0.01

NA = Not Analyzed

DESCRIPTION				
Sample Level (feet)	Ledge No.	Thickness (feet)	Lithology	Formation
163-164.5 162-163 161-162 160-161 159-160 158-159 157-158 156-157 155-156 154-155 153-154 152-153	14	12.5	Limestone, medium-light-olive-gray to light-olive-gray, very fine- to very coarse-grained, bioclastic (mainly micrite-enveloped grains), oolitic, peloidal; fossiliferous (crinoids, brachiopods, horn corals, and gastropods); in part micrograined limestone (silty and in part argillaceous) in basal foot and upper foot; few small nodules of medium-gray to grayish-black chert in interval 153-154 feet; traces of pyrite in upper foot; stylolites; thick-bedded to massive.	LOWER MEMBER OF NEWMAN LIMESTONE
151-152 150-151 149-150 148-149	13	4	Limestone, olive-gray to light-olive-gray, very fine- to coarse-grained (dominantly very fine- to fine-grained), bioclastic; in part greenish-gray to light-olive-gray and grayish-red, micrograined to very fine-grained limestone; traces of pyrite in basal foot; very thin to thin, irregular beds with grayish-red and dark-greenish-gray, silty, argillaceous laminations and shales.	TAGGARD RED MEMBER OF WILPOLT AND MARDEN (1959)
147-148 146-147 145-146 144-145 143-144	12	5	Limestone, olive-gray to medium-light-olive-gray, very fine- to coarse-grained, bioclastic (in part micrite-enveloped grains), peloidal, sparsely oolitic; stringers of dusky-yellowish-brown, micrograined limestone, with calcite birdseyes, in upper 3 feet; dark-reddish-brown and very dusky-red chert in interval 145-146 feet; traces of pyrite in upper foot; few stylolites; thin- to medium-bedded.	
142-143 141-142 140-141 139-140 138-139 137-138	11	6	Limestone, greenish-gray and light-olive-gray to olive-gray, micrograined, silty, in part with scattered birdseyes of crystalline calcite; in part fine- to very coarse-grained, peloidal calcarenite, slightly oolitic and bioclastic; sparsely fossiliferous (brachiopods and crinoids); thin- to medium-bedded; complexly interlaminated and interbedded with grayish-red and greenish-gray, silty shale; greenish-gray and grayish-red, indurated, calcareous shale in basal foot and upper foot.	
136-137 135-136 134-135 133-134 132-133 131-132 130-131 129-130 128-129 127-128 126-127	10	25	Limestone, light-olive-gray to light-gray, fine- to very coarse-grained, bioclastic (mainly micrite-enveloped grains), peloidal, oolitic; sparsely fossiliferous (crinoids, brachiopods, and horn corals); in part micrograined limestone in intervals 116-117, 121-122, and 128-129 feet, scattered traces of pyrite in lower 11 feet; stylolites; thick- to medium-bedded; crossbedded in upper 9 feet; few very thin, greenish-gray shales and argillaceous partings in intervals 112-113 and 116-117 feet. Thickness varies laterally.	LOWER MEMBER OF NEWMAN LIMESTONE

CHEMICAL ANALYSIS									
% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
97.09	1.06	1.10	0.19	0.11	0.04	0.04	99.63	NA	0.01
96.15	1.09	1.01	0.17	0.10	0.06	0.05	98.63		0.01
96.16	1.06	0.81	0.18	0.12	0.05	0.03	98.41		0.01
96.23	1.08	0.65	0.18	0.09	0.06	0.06	98.35		0.01
97.74	0.87	0.22	0.20	0.07	0.04	0.06	99.20		0.01
96.57	1.03	1.19	0.29	0.08	0.07	0.08	99.31		0.01
97.21	0.84	0.73	0.09	0.07	0.03	0.06	99.03		0.01
96.24	0.82	0.84	0.17	0.10	0.04	0.05	98.26		0.01
97.63	0.86	0.84	0.13	0.07	0.03	0.06	99.62		0.01
95.07	1.69	2.14	0.61	0.22	0.16	0.08	99.97		0.01
96.28	0.84	1.29	0.16	0.09	0.05	0.07	98.78		0.02
96.86	1.02	1.68	0.27	0.11	0.08	0.08	100.10		0.01
95.57	1.04	1.71	0.34	0.12	0.09	0.08	98.95		0.01
94.73	1.04	2.15	0.32	0.12	0.09	0.08	98.53		0.02
85.51	7.91	3.53	0.80	0.43	0.20	0.11	98.49		0.11
76.24	16.07	4.90	1.07	0.44	0.27	0.13	99.12		0.04
94.71	2.56	1.47	0.31	0.12	0.08	0.09	99.34		0.02
95.93	1.08	0.69	0.14	0.06	0.04	0.08	98.02		0.02
96.54	1.23	0.48	0.17	0.09	0.05	0.06	98.62		0.02
96.90	1.13	0.72	0.19	0.09	0.05	0.06	99.14		0.02
92.05	1.47	4.08	1.14	0.53	0.41	0.08	99.76		0.02
96.19	1.06	0.54	0.21	0.08	0.05	0.06	98.19		0.04
96.77	1.03	0.38	0.20	0.05	0.04	0.06	98.53		0.02
96.72	0.99	0.17	0.16	0.04	0.05	0.08	98.21		0.02
96.64	0.96	0.15	0.19	0.02	0.03	0.06	98.05		0.02
97.31	0.99	0.13	0.15	0.05	0.05	0.07	98.75		0.02
97.02	0.90	0.14	0.15	0.04	0.04	0.05	98.34		0.02
97.75	0.94	0.15	0.17	0.04	0.03	0.06	99.14		0.01
96.71	0.86	0.26	0.23	0.05	0.05	0.06	98.22		0.01
96.02	0.90	0.64	0.21	0.13	0.06	0.07	98.03		0.01
96.49	0.84	0.59	0.13	0.11	0.05	0.05	98.26		0.01
96.63	0.83	0.31	0.23	0.07	0.02	0.06	98.15		0.01
97.81	0.75	0.18	0.11	0.16	0.03	0.06	99.10		0.01
96.60	0.83	0.11	0.08	0.29	0.04	0.06	98.01		0.01
97.57	0.71	0.13	0.08	0.31	0.04	0.08	98.92		0.01
97.12	0.59	0.09	0.06	0.21	0.04	0.07	98.18		0.01
97.05	0.65	0.07	0.07	0.17	0.02	0.06	98.09		0.01
97.42	0.89	0.28	0.06	0.34	0.03	0.08	99.10		0.01
98.99	0.73	0.07	0.04	0.25	0.04	0.09	100.21		0.01
99.75	0.68	0.06	0.04	0.21	0.03	0.05	100.82		0.01
99.74	0.62	0.09	0.01	0.16	0.03	0.06	100.71		0.01
99.26	0.67	0.11	0.05	0.16	0.03	0.08	100.36		0.01
98.62	0.65	0.11	0.02	0.15	0.02	0.06	99.63		0.01
98.98	0.61	0.11	0.02	0.08	0.03	0.05	99.88		0.01
99.78	0.42	0.11	0.04	0.07	0.01	0.06	100.49		0.01
96.98	0.68	0.18	0.06	0.08	0.02	0.06	98.06		0.01
96.98	0.69	0.23	0.06	0.13	0.02	0.06	98.17		0.01
98.46	0.79	0.39	0.07	0.16	0.02	0.05	99.94		0.01

NA = Not Analyzed

DESCRIPTION				
Sample Level (feet)	Ledge No.	Thickness (feet)	Lithology	Formation
125-126				
124-125				
123-124				
122-123				
121-122				
120-121				
119-120	10	Continued		
118-119				
117-118				
116-117				
115-116				
114-115				
113-114				
112-113				
111-112			Limestone, medium-light-olive-gray, fine- to very coarse-grained, bioclastic (mainly micrite-enveloped grains), oolitic; sparsely fossiliferous (brachiopods and gastropods); medium-light-olive-gray to greenish-gray, microcrystalline to micro-grained limestone, in part dolomitic, slightly argillaceous, with abundant bioclastic grains, in basal foot and upper 2 feet; traces of pyrite in upper 2 feet; stylolites; medium- to thin-bedded; very thin, greenish-gray shale at base.	
110-111				
109-110	9	7		
108-109				
107-108				
106-107				
105-106				
104-105				
103-104				
102-103				
101-102				
100-101	8	10	Limestone, light-olive-gray to very light-gray, fine- to very coarse-grained, bioclastic (mainly micrite-enveloped grains), oolitic, peloidal; few stylolites; thick-bedded; 1-foot bed at top of ledge. Weathers very pale orange to light yellowish gray.	
99-100				
98-99				
97-98				
96-97				
95-96				
94-95				
93-94				
92-93				
91-92				
90-91				
89-90				
88-89				
87-88				
86-87	7	27	Limestone, very pale-orange to white, very fine- to very coarse-grained, bioclastic (mainly micrite-enveloped grains), oolitic, peloidal, with slightly earthy appearance; in part fossiliferous (crinoids, brachiopods, bryozoans, and gastropods); very finely crystalline dolomitic limestone, with bioclastic grains in interval 72-73 feet; few stylolites; thick-bedded to massive. Weathers very pale orange to light yellowish gray.	
85-86				
84-85				
83-84				
82-83				
81-82				
80-81				
79-80				
78-79				

LOWER MEMBER OF NEWMAN LIMESTONE

CHEMICAL ANALYSIS									
% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
98.79	0.64	0.18	0.04	0.09	0.03	0.07	99.84	NA	0.01
98.69	0.66	0.24	0.06	0.09	0.02	0.07	99.83		0.01
98.11	0.72	0.28	0.06	0.12	0.04	0.09	99.42		0.03
98.89	0.73	0.37	0.04	0.10	0.02	0.05	100.20		0.02
97.46	0.79	0.41	0.07	0.11	0.02	0.06	98.92		0.03
81.52	17.72	0.37	0.10	0.23	0.04	0.08	100.06		0.02
98.51	0.63	0.20	0.06	0.15	0.01	0.05	99.61		0.02
96.94	0.62	0.37	0.08	0.11	0.02	0.05	98.19		0.03
98.61	0.70	0.32	0.08	0.07	0.02	0.06	99.86		0.03
98.33	0.76	0.41	0.06	0.07	0.01	0.05	99.69		0.02
79.17	20.19	0.46	0.18	0.28	0.02	0.06	100.36		0.02
78.62	20.49	0.62	0.09	0.22	0.03	0.06	100.13		0.01
77.85	20.78	1.00	0.16	0.28	0.05	0.08	100.20		0.02
66.87	30.97	2.24	0.06	0.40	0.14	0.07	100.75		0.02
65.70	30.62	2.63	0.11	0.34	0.17	0.13	99.70		0.03
88.87	9.40	1.14	0.15	0.12	0.06	0.06	99.80		0.02
96.68	1.41	1.23	0.70	0.04	0.03	0.06	100.15		0.02
96.19	1.58	1.34	0.09	0.07	0.04	0.07	99.38		0.02
91.47	6.43	1.26	0.21	0.08	0.03	0.05	99.53		0.02
86.46	11.56	1.90	0.30	0.12	0.09	0.07	100.50		0.04
96.11	2.13	1.04	0.15	0.05	0.03	0.06	99.57		0.02
95.71	2.15	1.19	0.08	0.06	0.03	0.07	99.29		0.02
95.54	2.27	1.20	0.09	0.06	0.03	0.06	99.25		0.02
95.55	1.08	1.22	0.09	0.07	0.04	0.07	98.12		0.02
60.23	37.13	1.14	0.19	0.42	0.07	0.06	99.24		0.02
91.79	6.53	1.61	0.13	0.08	0.05	0.08	100.27		0.02
94.39	3.25	1.70	0.06	0.07	0.03	0.07	99.57		0.02
88.30	10.24	1.46	0.06	0.11	0.07	0.09	100.33		0.02
66.32	30.69	1.96	0.16	0.36	0.11	0.11	99.71		0.02
89.53	8.16	1.40	0.10	0.12	0.04	0.07	99.42		0.02
91.71	6.00	1.47	0.05	0.08	0.04	0.09	99.44		0.01
60.03	38.36	1.41	0.26	0.34	0.08	0.09	100.57		0.06
59.15	37.29	2.49	0.41	0.37	0.11	0.09	99.91		0.02
58.08	38.86	2.07	0.35	0.35	0.11	0.07	99.89		0.01
93.15	2.56	3.85	0.09	0.12	0.04	0.07	99.88		0.02
93.20	4.11	2.48	0.05	0.08	0.03	0.07	100.02		0.02
90.12	7.26	2.07	0.10	0.12	0.04	0.07	99.78		0.02
54.89	31.81	10.58	1.30	0.38	0.38	0.14	99.48	NOT ANALYZED	
53.01	30.39	14.08	1.48	0.51	0.34	0.13	99.94		
54.52	27.93	14.67	1.84	0.45	0.50	0.12	100.03		
65.22	26.13	6.97	1.09	0.35	0.29	0.10	100.15		
69.07	21.35	7.10	1.12	0.37	0.32	0.12	99.45		
65.71	24.46	8.27	1.03	0.34	0.29	0.12	100.22		
74.29	11.97	11.28	1.22	0.34	0.31	0.18	99.59		
84.47	7.62	6.30	0.84	0.42	0.27	0.17	100.09		
87.18	3.91	6.03	0.79	0.47	0.23	0.13	98.74		
85.28	4.34	8.40	1.00	0.47	0.19	0.15	99.83		
79.45	7.74	10.42	1.60	0.60	0.37	0.19	100.37		

NA = Not Analyzed

DESCRIPTION

Sample Level (feet)	Ledge No.	Thickness (feet)	Lithology	Formation
77-78				
76-77				
75-76				
74-75				
73-74	7—Continued			
72-73				
71-72				
70-71				
69-70				
68-69				
67-68				
66-67	6	5	Dolomitic limestone, very light-olive-gray to grayish-orange, very finely crystalline, with varied amounts of bioclastic grains; sparsely fossiliferous (brachiopods); light-olive-gray to yellowish-gray, earthy, very finely crystalline dolomite in lower 2 feet; small vugs filled with quartz and calcite in interval 64-66 feet; thick-bedded.	
65-66				
64-65				
63-64				
62-63				
61-62				
60-61				
59-60	5	9	Limestone, very light-gray to light-olive-gray, very fine- to very coarse-grained, bioclastic (mainly micrite-enveloped grains), slightly oolitic and peloidal; fossiliferous (crinoids and brachiopods); locally grades into microcrystalline to very finely crystalline dolomite with varied amounts of bioclastic grains; traces of pyrite in interval 59-60 feet; stylolites; thick-bedded.	
58-59				
57-58				
56-57				
55-56				
54-55				
53-54				
52-53				
51-52				
50-51				
49-50				
48-49	4	13	Limestone, very light-gray to light-olive-gray, very fine- to very coarse-grained, bioclastic (mainly micrite-enveloped grains), slightly oolitic and peloidal; fossiliferous (crinoids, brachiopods, and gastropods); zones of very light-olive-gray, slightly earthy, very finely crystalline dolomite; few stylolites; thick-bedded.	
47-48				
46-47				
45-46				
44-45				
43-44				
42-43				
41-42				
40-41				
39-40				
38-39	3	14	Dolomitic limestone and dolomite, olive-gray and light-olive-gray to very light-gray, microcrystalline to very finely crystalline, silty, slightly argillaceous; in part micrograined limestone, with sub-conchoidal fracture; zones of very fine- to coarse-grained, bioclastic calcarenite in basal and middle parts; traces of pyrite; thick-bedded.	
37-38				
36-37				
35-36				
34-35				
33-34				
32-33				
31-32				
30-31				

LOWER MEMBER OF NEWMAN LIMESTONE

Low-Silica and High-Calcium Stone in the Newman Limestone on Pine Mountain

CHEMICAL ANALYSIS									
% CaCO ₃	% MgCO ₃	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% K ₂ O	% Na ₂ O	% Total	% P	% S
81.87	7.07	7.92	1.23	0.50	0.28	0.18	99.05	NOT ANALYZED	
77.20	13.67	7.97	0.94	0.42	0.22	0.17	100.59		
75.72	18.99	3.03	0.49	0.37	0.04	0.11	98.75		
67.99	6.97	21.91	0.74	0.54	0.22	0.16	98.53		
56.77	0.74	41.51	0.05	0.45	0.12	0.11	99.75		
79.12	3.48	15.11	0.66	0.32	0.20	0.13	99.02		
77.85	4.83	14.47	0.68	0.34	0.20	0.14	98.51		
78.20	4.55	14.41	0.53	0.27	0.17	0.13	98.26		
75.96	4.06	18.11	0.91	0.41	0.25	0.15	99.85		
82.86	3.57	11.60	0.71	0.30	0.20	0.15	99.39		
66.49	7.74	21.40	1.45	0.56	0.42	0.17	98.23		
81.65	6.92	7.73	1.44	0.47	0.41	0.18	98.80		
75.31	4.77	17.41	0.85	0.43	0.22	0.06	99.05		
71.85	7.77	16.91	1.60	0.60	0.43	0.20	99.36		
87.30	3.63	5.99	1.20	0.40	0.33	0.15	99.00		
89.10	2.04	6.22	1.23	0.42	0.31	0.18	99.50		
81.47	1.68	15.96	0.91	0.39	0.24	0.15	100.80		
81.94	5.03	9.30	1.73	0.71	0.48	0.22	99.41		
73.97	6.32	14.21	2.41	1.11	0.67	0.26	98.95		
82.77	3.54	11.08	1.83	0.77	0.50	0.24	100.73		
81.53	1.89	13.23	1.38	0.57	0.36	0.17	99.13		
74.58	3.14	15.75	3.08	1.26	0.86	0.28	98.95		
78.34	6.06	12.22	1.89	0.82	0.53	0.20	100.06		
73.77	2.00	17.60	2.92	1.36	0.82	0.24	98.71		
74.66	2.18	17.93	3.08	1.38	0.89	0.24	100.36		
77.16	2.16	15.15	2.98	1.26	0.86	0.26	99.83		
40.89	1.64	50.07	3.34	1.61	1.04	0.22	98.81		
88.89	1.76	5.43	0.88	0.64	0.25	0.15	98.00		
87.70	2.28	7.46	1.22	0.67	0.31	0.16	99.80		
82.10	2.62	10.28	1.81	0.88	0.45	0.20	98.34		

DESCRIPTION

Sample Level (feet)	Ledge No.	Thick-ness (feet)	Lithology	Formation
29-30 28-29 27-28	3—Continued			
26-27 25-26 24-25 23-24 22-23 21-22 20-21 19-20 18-19 17-18 16-17 15-16 14-15 13-14 12-13 11-12 10-11 9-10 8-9 7-8 6-7 5-6 4-5 3-4	2	24	Limestone, olive-gray, micrograined to very finely crystalline, with scattered bioclastic grains (in part silicified), in part with sub-conchoidal fracture; argillaceous in lower part; sparsely fossiliferous (brachiopods, crinoids, horn corals, echinoids, and bryozoans; in part silicified); greenish-gray argillaceous limestone in basal foot; abundant chert (multicolored; commonly color banded) in nodules, discontinuous beds, and irregular bodies; traces of glauconite; few stylolites; medium- to thin-bedded, with thin shales and argillaceous partings. Thickness varies laterally.	LOWER MEMBER OF NEWMAN LIMESTONE
2-3 1-2 0-1	1	3	Limestone, dark-olive-gray and olive-gray to brownish-gray, micrograined to very finely crystalline, silty, slightly argillaceous, with few bioclastic grains; subconchoidal fracture; fossiliferous (crinoids, brachiopods, and echinoids); abundant algal oncolites in lower 2 feet; calcite-filled veinlets in upper foot; medium-bedded.	

BASE OF SAMPLED SECTION AND TOP OF GRAINGER FORMATION

Upper part of Grainger consists of gray to greenish-gray, silty shale, with scattered sideritic concretions.

APPENDIX B:

DETERMINATION OF TOTAL SILICA IN THE STUDY SAMPLES¹

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INTRODUCTION

The most critical parameter for the assessment of limestone for potential use as mine rock dust is total silica (SiO_2) content. Very finely ground rock dust may be respired, and hence, the silica content must be limited to minimize the potential silicosis hazard.

The amount of free and combined silica in rock dust is specified by Federal statute (Public Law 91-173, Section 318(d)) to be not more than a total of 4 percent by weight (Federal Register Office, 1970). The Mine Safety and Health Administration (MSHA) is responsible for monitoring the quality of rock dust used in the United States. Thus, the measurement of silica in limestone used for rock dust must be accurate and comparable to the measurement obtained by MSHA procedures.

The approved MSHA standard for rock dust is presented in the American Society for Testing and Materials (ASTM) Standard Specification C 737-73 (American Society for Testing and Materials, 1983a). The procedure for the analysis of silica in rocks under this standard is ASTM Method C 25-83 (American Society for Testing and Materials, 1983b). The procedure is a gravimetric determination, and has the advantage of providing good precision and accuracy, with low set-up costs. However, it has the decided disadvantage of being a very slow and labor-intensive procedure, with an average production of eight samples per 12 man hours (William McKinney, personal commun., 1981). This rate of analysis would be prohibitive for this study, which involves the analysis of hundreds of samples.

In addition to gravimetry, common methods for the determination of silica in limestone include (1) acid digestion followed by analysis, using atomic absorption or photometry, (2) X-ray fluorescence determination (on pressed powders or fused lithium borate-limestone disks), and (3) neutron activation analysis. X-ray fluorescence and neutron activation are rapid methods that provide good accuracy and precision, but have the disadvantage of requiring very expensive equipment and highly trained operators. Atomic absorption does not provide results of sufficient reliability, particularly for

samples with low silica concentrations, due to matrix effects and the difficulty in reducing a tetra-valent element like silicon to a resonance state.

For this study, the silica determination method was based on a lithium borate-sample fusion technique, followed by acid digestion and subsequent determination by photometry. This method was modified after the method of Shapiro (1975); additional discussion may be found in Kolthoff and Sandell (1952). Shapiro's method is based upon a NaOH flux of the sample, and has a final sample solution concentration of 50 ppm. To obtain optimum results for limestones with low silica contents, a higher concentration is required. A 2000 ppm solution is used here. Since silica may polymerize at concentrations above approximately 100 ppm (Brown and others, 1970), a depolymerization step (dilution followed by the addition of NaOH) was added.

When properly calibrated, the above method offers high precision and accuracy, along with high sample output, and utilizes only moderately priced equipment. Comparison of analyses made on replicate samples by this method and by the MSHA laboratory found good agreement (Table B1).

TECHNIQUE FOR SILICA ANALYSIS OF CARBONATE ROCKS

The procedures described in this report are based upon a lithium borate fusion of the sample and subsequent dissolution of the bead in nitric acid. The use of lithium borate fusion for this type of analysis has become common in recent years (for example, see Muter and Nice, 1975). A 2:1 flux mixture of lithium tetra-borate to lithium meta-borate is used to provide an acid flux, which facilitates removal of samples with high iron concentrations from the carbon crucibles. The borates may be purchased pre-mixed from chemical companies. Various manufacturers' products were used in the study, and all were found to have low-level Na or K contamination, and it is recommended that standards and samples be prepared with the same batch of flux if these elements are to be determined. The standard purity crucibles used in the procedure were obtained from SPEX Industries. The

¹Any use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the Center for Applied Energy Research or the Kentucky Geological Survey.

crucibles were checked, and potential contamination was found to be insignificant. The procedure produces a solution of 2000 ppm sample.

Table B1.—Comparison of Silica Content for Samples Analyzed by the MSHA Method and by the Procedure of This Study.

Sample	SiO ₂ Content		Notes
	KCERL	MSHA	
STG-1	0.9	0.6	1
BCS-368	0.9	0.9	2
NBS-88a	1.3	1.4	3
BAO-2	4.4	4.4	1
BAG-1	6.0	6.1	1
BAO-1	9.4	9.3	1
WC-1	10.2	9.5	1

1. Replicate analysis (10 determinations) of this in-house secondary standard resulted in a coefficient of variation (standard deviation/mean X 100) of 1 to 5 percent for the technique used for this report. McKinney (personal commun., 1981) estimated an overall accuracy of 4 percent and a precision of 0.1 for values in the 1 to 5 percent SiO₂ range for the MSHA technique.

2. British Bureau of Analyzed Samples Certified Value = 0.92 percent SiO₂.

3. National Bureau of Standards Provisional Value = 1.20 percent SiO₂.

Fluxing Procedure

Reagents

- 2:1 mixture of lithium tetra-borate to lithium meta-borate.

Procedures

- Weigh out 1.2 grams of lithium borate flux into clean carbon crucibles.
- Weigh out 0.2 gram of sample. An exact measurement of weight is essential; a variation of 5 to 10 percent of the total amount is acceptable.
- Make a crater in the flux mixture and pour the sample into it. Carefully stir the sample and flux together with a dissecting needle, being careful not to scrape the bottom and sides of the crucible too much.
- Place the crucible in a pre-heated muffle furnace at 1000°C for 30 to 35 minutes.
- After the samples have been removed and cooled, remove the fused beads from the crucibles and place them in 125-ml (4-oz.) polyethylene bottles. Check the crucible to insure that no splatter of sample remains.

- Add approximately 40 ml of hot distilled-deionized water, a 1-inch Teflon stir bar, and 5 ml of 1:1 HNO₃ to the plastic bottles. Place the bottle on a stirrer-heater and set at a low heat to prevent melting of the bottle. Stir until bead is dissolved.
- After the bead is dissolved, transfer the contents to a 100-ml volumetric flask, rinsing the bottle several times with distilled-deionized water. Fill the flask with water.
- Filter the sample to remove the residual carbon from the crucibles. Paper filters were found to add Na to the samples. For this analysis, 0.45-micron membrane filters and vacuum apparatus were used.

Determination of Silica in Carbonate Rocks

Reagents

- Complexer Ammonium molybdate, 15 gr/liter
- Suppressor Tartaric acid, 40 gr/liter (4%)
- Depolymerizer NaOH, 40 gr/liter (1.0 N)
- Acidifier HCl, 100 ml/liter (1.14 N)
- Reducer 0.7 gr sodium sulfite + 9.0 gr sodium bisulfite + 0.15 gr 1-amino 1-naphthol-4-sulfonic acid/liter

The reducing and complexing solution should be made fresh for each run. The tartaric acid solution should be checked periodically for bacterial growth, which can cloud this reagent.

Procedures

- Add 2 ml of sample to a series of 100-ml plastic bottles or flasks, along with a set of standards and a blank.
- Add 20 ml of distilled water with a precision dispenser such as a Repipet or Oxford Diluter. (All reagents should be dispensed using this type of equipment; transfer pipets are too slow and dangerous for this type of procedure.)
- Add 2 ml of the 1.0 N NaOH; cap and shake; let stand for 2 hours.
- Add 3 ml of 1.14 N HCl; cap and shake; let stand 10 minutes.
- Add 10 ml of ammonium molybdate solution; cap and shake; let stand for 50 minutes.
- Add 10 ml of tartaric acid; swirl.
- Add 10 ml of reducing solution; cap and shake; let stand 1 hour. Solution should be stable for the remainder of the day.
- Zero spectrophotometer with a blank; run standards and samples at a wavelength of 700 nm.

Data Reduction and Standardization

Silica concentration is determined from a working curve prepared with standard solutions. The curve is

found to be essentially linear throughout, and, with the solution concentrations in this study, covers concentrations ranging from 0 to 200 ppm or 0 to 10 percent SiO_2 in the rock (see Table B1). The rating curve is in practice determined from a linear regression of the standard data using a slide rule calculator.

Standards used for the determination include the National Bureau of Standards (NBS) 1c argillaceous limestone and NBS 88a dolomite (Cali, 1978; Meinke, 1967), and the British Chemical Standards (BCS) No. 368 dolomite (Ridsdale, 1971). Additional standards were made by spiking high-purity CaCO_3 with U.S. Geological Survey silicate rock standards (Flanagan, 1976). A secondary set of in-house standards were then made from replicate determinations.

Comparison With MSHA Analyses

A series of blind determinations were made on reference samples used in this study by William McKinney of the Mine Safety and Health Administration (MSHA) Laboratory at Mount Hope, West Virginia, using their procedures. These data, along with determined concentrations from this study, are presented in Table B1. The results are in remarkable agreement, with the only significant differences found for the samples with the highest and lowest concentrations. Thus, the silica data from the analytical techniques used in this study are sufficient to identify, with a high degree of confidence, limestone deposits that qualify as feedstocks for the production of mine rock dust.