GEOLOGICAL SURVEY CIRCULAR 774

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March 3, 1849

Reconnaissance Investigation of High-Calcium Marble in the Beaver Creek Area, St. Lawrence County, New York

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By C. ERVIN BROWN

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CONTENTS

ILLUSTRATIONS

TABLES

Reconnaissance Investigation of High-Calcium Marble in the Beaver Creek Area, St. Lawrence County, New York

By C. ERVIN BROWN

ABSTRACT

Three belts of marble of the Grenville Series were mapped in the Beaver Creek drainage basin, St. Lawrence County, N.Y. One of these, on the west side of Beaver Creek, consists of coarsely crystalline pure calcitic marble that occurs in a zone at least 10 by 0.8 km in extent. Samples of marble show $CaCO_3$ content to be greater than 93 percent, and some samples contain greater than 96 percent, and only small amounts of MgO and Fe_2O_3 are present. Marble in two other belts to the east of Beaver Creek are variable in composition, but locally have high content of calcium carbonate material.

The marble deposit west of Beaver Creek has a chemical composition favorable for specialized chemical, industrial, and metallurgical uses. Another favorable aspect of the deposit is its proximity to inexpensive water transportation on the St. Lawrence Seaway only 27.5 km away by road, at Ogdensburg, N.Y.

INTRODUCTION

Limestone and other carbonate rocks are among the most widely-used mineral commodities in the world. These rocks have many uses in construction and agriculture and for chemical and metallurgical purposes. Suitable carbonate rocks for use in construction generally are sought close to the market because of high transportation costs. Low-purity limestone and dolomite are widely distributed in the United States, and generally a source can be found close to the consumer. However, high-calcium limestone[1] suitable for chemical, metallurgical, and some other specialized uses is far more scarce and, consequently, its higher value causes transportation costs to be a smaller factor in its exploitation (Hubbard and Ericksen, 1973).

Metasedimentary rocks of the Grenville Series in the St. Lawrence lowlands northwest of the Adirondack Mountains include much marble that is potentially a resource of high-purity carbonate rock. Some of these marble units have been described previously by Cushing and Newland (1925), Buddington (1934), Brown and Engel (1956), Prucha (1953) and Brown (1969). Many of the marble units are impure, containing abundant silicate minerals or quartz, and locally they contain thin disrupted layers of rusty, biotitic gneiss, quartzo-feldspathic rocks, and quartzite. Some units, however, are high-purity carbonate rocks. Unfortunately, the studies of these units have given little attention to their potential as sources of high-calcium limestone. Only a few chemical analyses of the marbles have been published (Buddington, 1934, p. 219), and these are of uncertain areal significance.

Some local marbles have been used in the past mainly for construction purposes. Quarries a short distance southwest of Gouverneur, N.Y. (fig. 1), were operated in the 1800's and early 1900's for marble dimension stone. Buildings, monuments, and sidewalks made from this light-gray marble are seen throughout the re-

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[1] High-calcium limestone is rock having 95 percent $CaCO_3$ content or greater, and those with greater than 97 percent $CaCO_3$ are called ultra-high calcium limestone (Carr and Rooney, 1975). High-purity carbonate rock contains more than 95 percent combined $CaCO_3$ and $MgCO_3$, and high-magnesian dolomite has more than 43 percent $MgCO_3$. A few uses of high-calcium limestones are for blast furnace and open hearth flux, and in the manufacture of glass, cement, alkalis, and alumina (Lamar and Willman, 1938). Other chemical specifications for these special uses are as important as the carbonate content. For instance, high calcium limestone used in the manufacture of alumina must have less than 0.5 percent sulfur and phosphorus. Limestone used in the manufacture of glass must have a uniform high-carbonate content and contain less than 0.1 percent Fe_2O_3. Cement manufacture and most flux uses require less than 3 percent $MgCO_3$ in the raw material. Another important use of pure limestone is as a white filler in a variety of manufactured products such as paint, rubber, flooring, plastics, and paper. The principal requirements for use as a filler are high whiteness and ease of grinding to a fine, soft powder.

gion. Marble for lime-burning, crushed stone, and furnace flux was produced in the past from quarries near Richville (Cushing and Newland, 1925). However, for the past 30 to 40 years marble has been produced only for crushed stone and agricultural limestone from a quarry south of Gouverneur, and at the present time also from a quarry north of Gouverneur where an additional product—bagged, white, dolomitic, marble chips for landscaping purposes—is also produced. Except for the latter, these uses of limestone require the supply to be close to the market because of transportation costs. Consequently, because only a small local market exists, the vast resource of carbonate rocks here is underutilized.

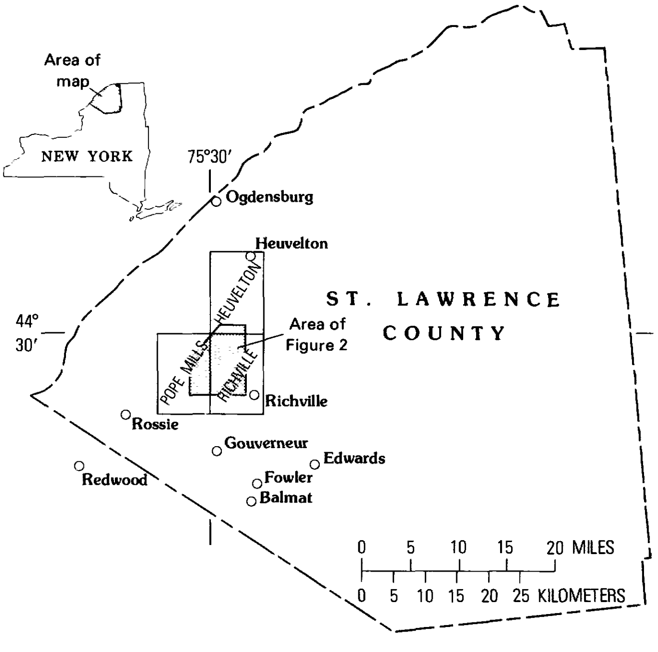


FIGURE 1.—Index map of St. Lawrence County, N.Y., showing area of this investigation.

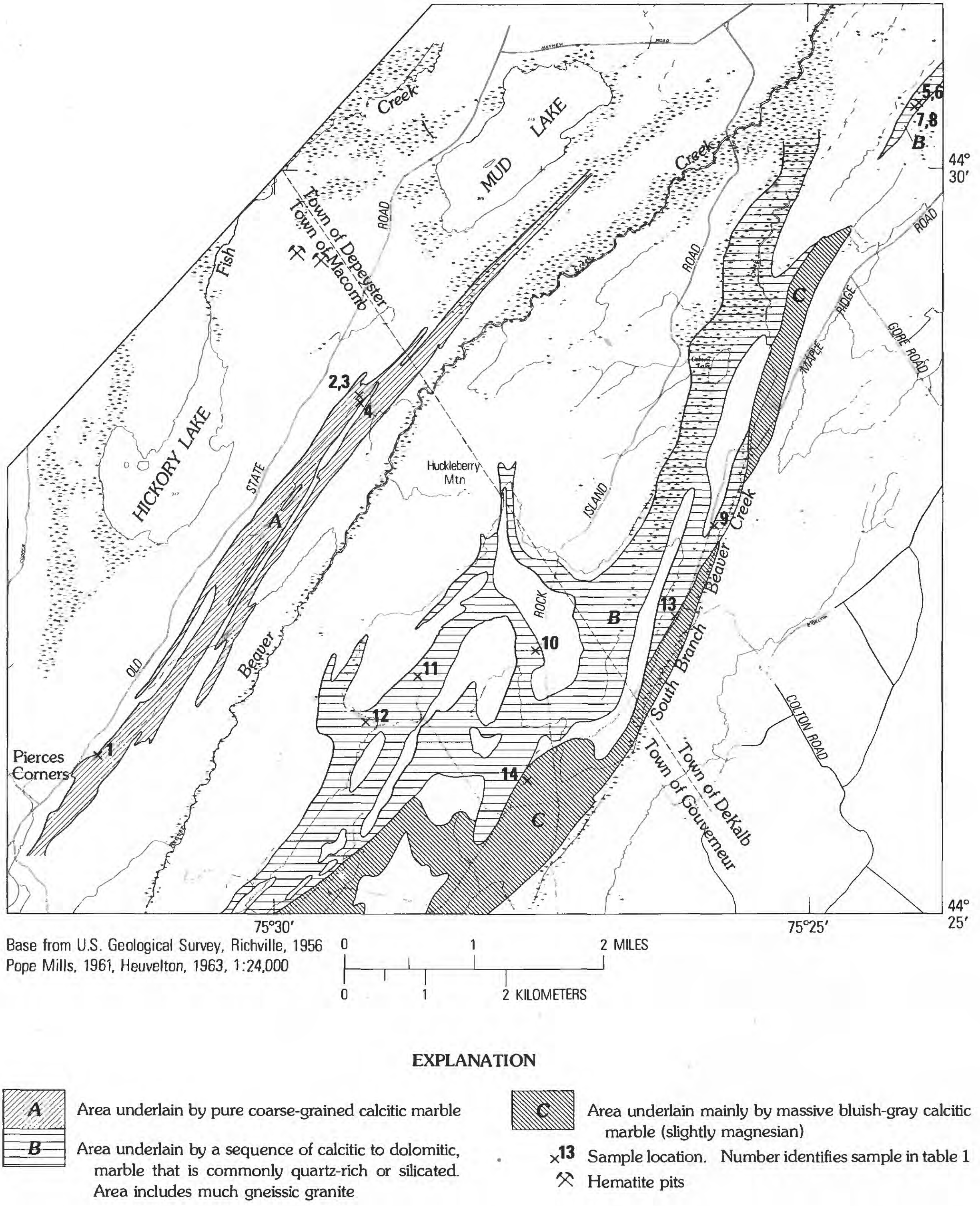
While doing detailed geologic mapping of an area northwest and southeast of Beaver Creek in St. Lawrence County from 1967 to 1971, the author mapped three belts of marble (fig. 2), one of which appeared to be an essentially pure calcitic marble and the other two locally appeared to contain some high-purity calcitic marble. Chemically analyzed grab samples indicated that some of these marbles do have unusually high $CaCO_3$ content. Additional sampling, however, was needed to evaluate the rock as a high-calcium limestone resource. In 1975, the author assisted by Harold Hubbard and Ken Books, of the U.S. Geological Survey, sampled marble at two localities with a portable core drill. Analyses from these samples prove that one extensive belt of pure calcitic marble west of Beaver Creek contains rock that chemically qualifies for specialized uses. A less extensive deposit of similar rock is east of Beaver Creek. Convenient and inexpensive water transportation on the St. Lawrence Seaway enhances the possibility that the deposits could be exploited economically.

DESCRIPTION OF MARBLE BELTS IN THE BEAVER CREEK DRAINAGE BASIN

MARBLE OF UNIT A

Belt *A* (fig. 2) consists of coarsely crystalline marble in which calcite grains are as much as 2.5 cm across, and average about 1.5 cm. The rock has the textural appearance of rock candy or very coarse rock salt, and locally shows flow banding that is outlined by graphite specks and other fine-grained accessory minerals. This marble unit is surrounded by impure carbonate rocks that contain numerous rusty-weathering biotite gneiss and quartzite layers. These thin layers are more brittle than the enclosing marble and are disrupted by differential tectonic flowage. Many of the impure carbonate-bearing rocks are better named "carbonate gneisses" rather than marble. Rocks west of Beaver Creek, including marble *A*, are folded and in turn refolded. The linear pattern of this belt on figures 3 and 4 is an expression of tight, nearly isoclinal, folding that has produced a northeastward strike and dips that are generally greater than 50° either to the northwest or to the southeast. At the sample sites on figures 3 and 4 the layering has a strike of N. 50 E. and dip of 70° to 75° SE. The hook-shaped patterns of the margins and the short linear areas of rock, other than marble, along the axial crests or troughs of folds is an interference pattern produced by cross-folds nearly transverse to the northeast trends. One can infer from the steep attitudes of the carbonate rocks that similar lithologies extend downward, certainly beyond practical mining depths.

Topographically, the area that includes marble belt *A* is characterized by low, linear, and essentially parallel ridges. The pure coarse



Base from U.S. Geological Survey, Richville, 1956
Pope Mills, 1961, Heuvelton, 1963, 1:24,000

EXPLANATION

A Area underlain by pure coarse-grained calcitic marble

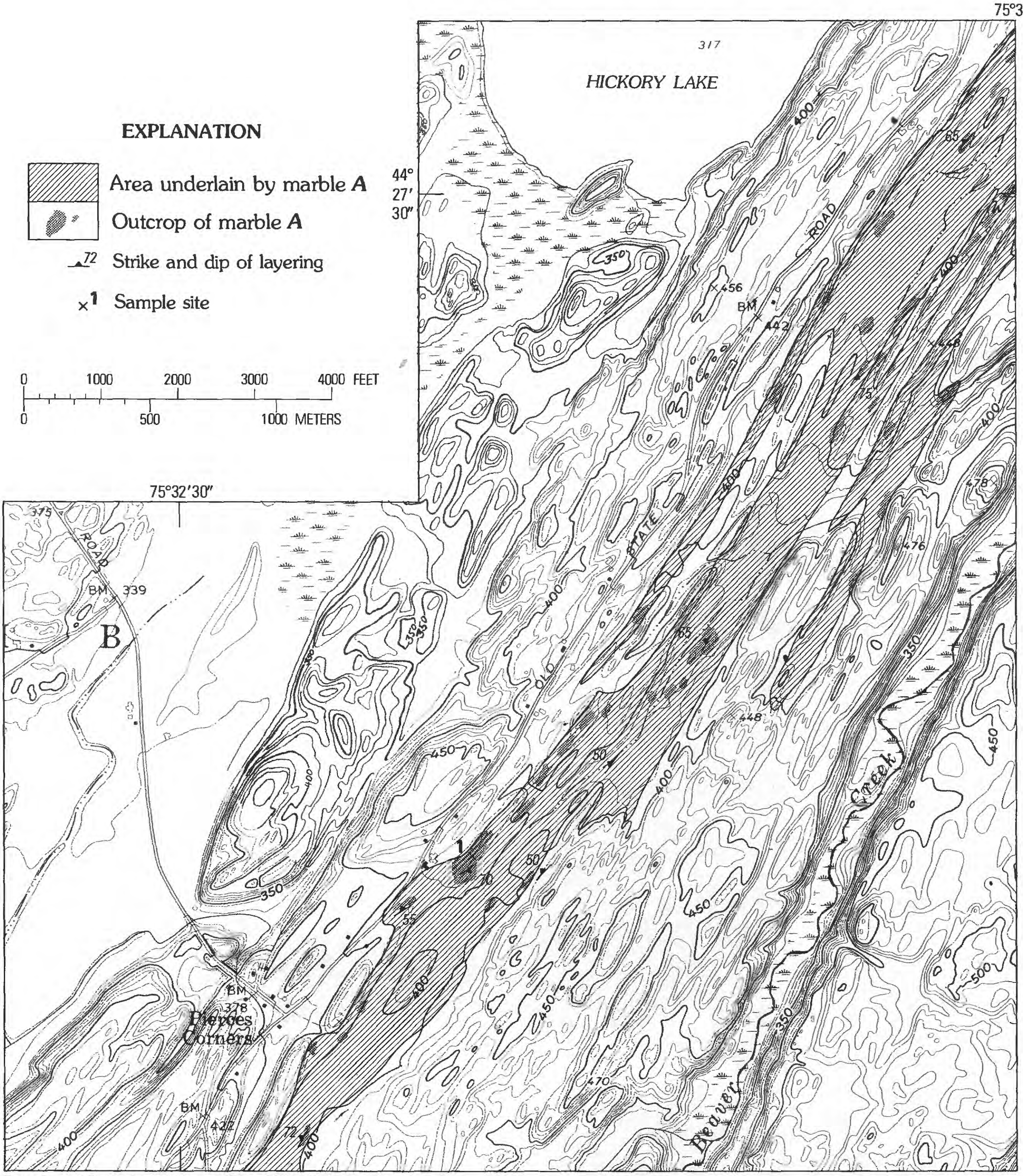
B Area underlain by a sequence of calcitic to dolomitic, marble that is commonly quartz-rich or silicated. Area includes much gneissic granite

C Area underlain mainly by massive bluish-gray calcitic marble (slightly magnesian)

×13 Sample location. Number identifies sample in table 1

⚒ Hematite pits

FIGURE 2.—Marble belts in part of the Beaver Creek drainage basin, St. Lawrence County, N.Y. Area of this map shown on figure 1.



Base from U.S. Geological Survey, Pope Mills, 1961

FIGURE 3.—Sample sites and outcrops in southwestern part of marble belt *A*.

marble forms the low areas and thus is easily located because it underlies the main broad valley bottom in the area between Old State Road and Beaver Creek. This marble has fewer outcrops than the impure ridge-forming lithologies, but protrudes through the valley fill as large areas of pavement outcrops at enough places to verify its presence. Regionally, most of the valleys are filled by postglacial lacustrine sediments, chiefly sticky gray clay, which is known to be locally more than 15 m thick where drilled in nearby valleys. This clay is a potential source of the alumina needed for the production of cement, and the required Fe_2O_3 is available from an iron-mineralized zone close to an outlier of Potsdam Sandstone a short distance to the north (fig. 4) or from other nearby iron mines such as at Star Lake, N.Y.

MARBLE OF UNITS B AND C

Unit *B* consists of pure to impure calcitic to dolomitic marble. The calcitic marble is coarsely crystalline (0.5 to 1 cm) and disintegrates readily to crumbly calcite debris. Zones of quartz-rich calcitic marble are common. The dolomitic marble is gray, and contains thin discontinuous layers of diopside and tremolite. Locally, the upper part of unit *B* is rich in talc (Brown, 1969). Many extensive lenses of quartz, plagioclase gneiss, and granitic gneiss, also occur in unit *B*. Although marble in this unit sampled at localities 5 to 8 (fig. 2) contains high-calcium carbonate, its most characteristic lithology is quartz-bearing or silicate-rich marble.

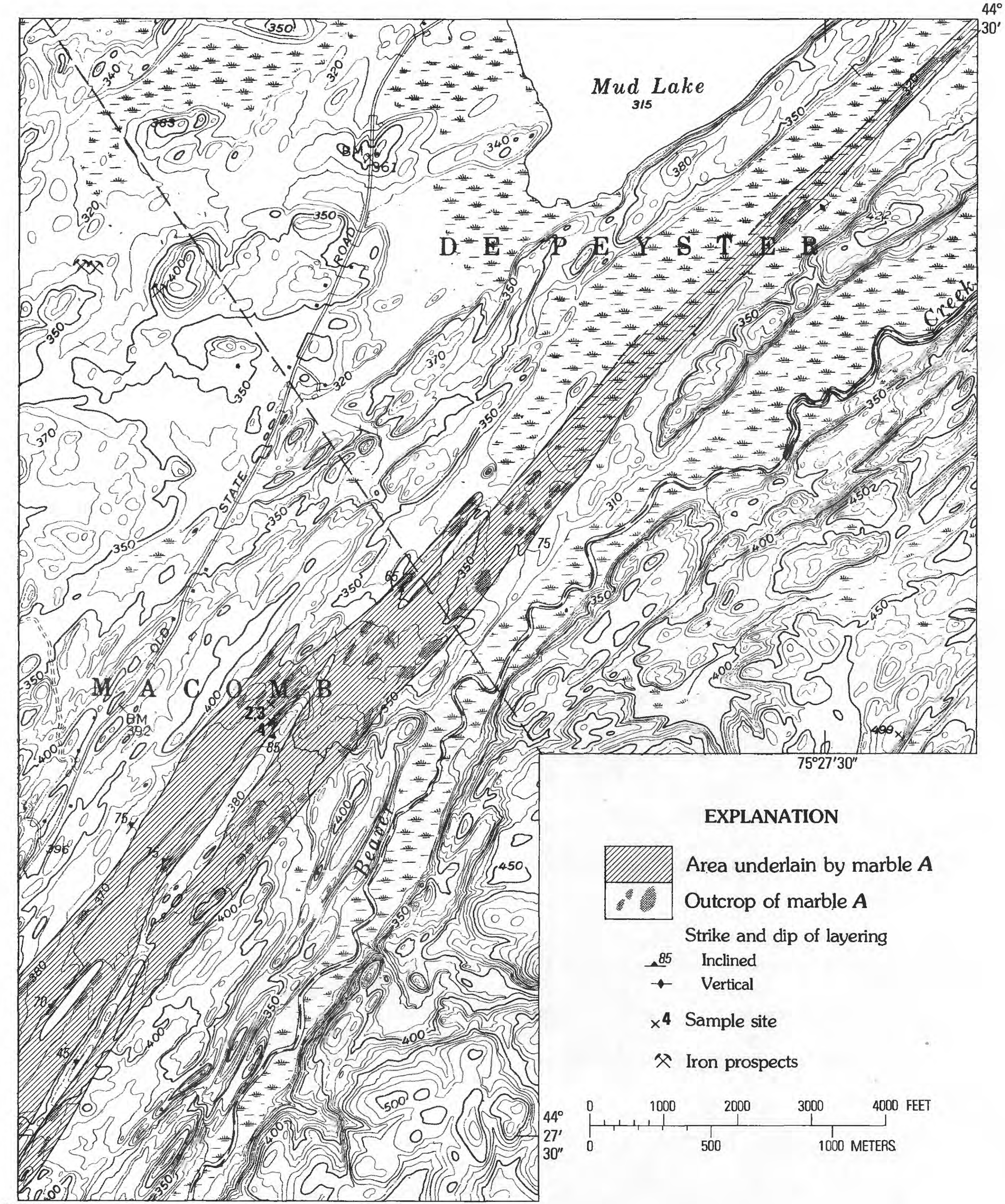
Marble from unit *C*, in contrast to that of unit *B*, has much more uniform lithology. It generally is massive, coarse-grained, and calcitic, and contains accessory tremolite, graphite, and phlogopite. Tremolite occurs as distinct, sparse, randomly distributed narrow prisms as much as 3-cm long that weather in relief on the outcrop. The topographic expression of these two marble units is also different. Marble *B* is generally dolomitic and easily disintegrated and underlies low areas in which large granitic gneiss lenses form elongate steep-sided knobs. Marble *C*, is more massive and uniform and forms gentle-sloped upland areas with low local relief.

The geologic structure of the area between Beaver Creek and the South Branch of Beaver Creek, including marble units *B* and *C*, is a southeastwardly recumbent antiform. Marble unit C is the structurally lowest unit and occupies the axial part of the fold. Unit *B* lies above *C* and is mainly exposed in the upper limb of the recumbent antiform. The dip of the axial plane of the fold ranges from moderately northwestward in the northeast part of the area to nearly horizontal near North Gouverneur.

DISCUSSION OF ANALYTICAL RESULTS

Chemical analyses of samples collected from marbles *A* and *B* in the second phase of sampling (Nos. 3, 4, 6, 7, 8, table 1 and fig. 2) generally agree with the high $CaCO_3$ content previously shown by samples 2 and 5 of grab samples taken earlier from the same localities. Sample 1, taken 4 miles southwest of location of samples 2, 3, and 4 (fig. 2), is almost identical to them chemically and supports field observations indicating that the marble in belt *A* is of high purity and lithologically similar throughout its extent. Although one can infer from a cursory examination of the analyses of marbles *A* and *B* that they are high-calcium limestones, determining the actual $CaCO_3$ content of a marble from its analysis is not that simple. Most metamorphosed limestones contain some calcium-magnesium silicates such as tremolite and diopside. Phlogopite, a mica containing magnesium, is also generally present. As a consequence, the CaO and MgO is not only in calcite and dolomite but also in silicate minerals. Determining the approximate $CaCO_3$ content is possible using a system similar to, but simpler than, determining normative mineral percentages of an igneous rock.

First, one must determine what silicate minerals are present. This can be done petrographically, or by dissolving the carbonate and identifying the insoluble minerals, or by deduction from the chemical analysis—or by a combination of these. Phlogopite contains, among other elements, potassium and aluminum. If the analysis shows significant quantities of these elements one should calculate percentage of phlogopite present. However, since phlogopite has no calcium, it has no effect on the amount of CaO available for the carbonates and, therefore, can be ignored for the purpose of determining the $CaCO_3$ content. The presence of calcium-magnesium silicates, diopside or tremolite, does affect the interpretation of the analyses, and the relative amounts of each should be known because diopside is 26 percent CaO,



Base from U.S. Geological Survey, Richville, 1956

Figure 4.—Sample sites and outcrops in northeastern part of marble belt *A*.

TABLE 1.—*Chemical analyses of marbles in Beaver Creek drainage basin, St. Lawrence County, N.Y.*

[Samples 1, 3, 4, 6, 7, and 8 analyzed by method described under "single solution" in U.S. Geol. Survey Bull. 1401. Analyst: Z. A. Hamblin. Samples 2 and 5 analyzed by method described in U.S. Geol. Survey Bull. 1144-A, supplemented by atomic absorption method. Analysts: P. Elmore, J. Kelsey, G. Chloe, H. Smith, J. Glenn. Samples 9–14 analyzed by method described in U.S. Geol. Survey Prof. Paper 575-B, p. 187–191. Analysts: P. Elmore, S. Boots, W. Curtis, J. Glenn, H. Smith, J. Kelsey]

Lab. No.	W190983	W174851	W190981	W190982	W174852	W190978	W190979	W190980	W171816	W171817	W171818	W171821	W171820	W171819
Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Marble unit	A	A	A	A	B	B	B	B	B	B	B	B	C	C
SiO_2	0.99	0.42	0.40	0.89	2.2	2.4	4.1	5.0	1.1	1.4	1.5	10.4	0.34	1.8
Al_2O_3	.00	.22	.00	.00	.31	.09	.00	.39	.08	.11	.28	1.6	.08	.00
Fe_2O_3	.00	.00	.00	.00	.00	.05	.01	.05	.10	.05	.17	1.5	.17	.15
FeO	.04	.05	.04	.04	.15	.04	.04	.04	.28	.04	.16	.72	.16	.24
MgO	.88	.53	.87	1.7	1.1	.81	1.5	1.2	20.4	2.4	4.0	7.6	3.70	3.5
CaO	55.4	53.7	55.0	55.5	52.5	55.2	55.3	53.4	30.0	51.0	49.3	38.5	49.9	49.7
Na_2O	.00	.00	.00	.03	.00	.03	.01	.01	.00	.04	.10	.28	.03	.04
K_2O	.01	.05	.01	.03	.03	.01	.05	.19	.00	.12	.20	.41	.00	.12
H_2O+	.39	.32	.20	.34	.39	.33	.34	.34	.00	.00	.03	.11	.03	.02
H_2O-	.06	.07	.04	.05	.07	.07	.06	.07	1.1	1.3	.66	.90	.94	1.2
TiO_2	.01	.00	.01	.02	.02	.02	.02	.03	.00	.00	.00	.10	.00	.00
P_2O_5	.02	.00	.01	.02	.00	.00	.03	.04	.04	.07	.09	.29	.04	.02
MnO	.00	.00	.00	.00	.00	.00	.00	.01	.05	.05	.07	.09	.08	.02
CO_2	42.9	43.6	42.8	42.6	42.4	42.4	39.3	39.4	46.4	43.4	43.5	33.9	44.4	43.3
SO_3	[1] n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.5	n.d.	n.d.
Sum	100.7	99.0	99.4	101.2	99.2	101.5	100.8	100.2	99.6	100.0	100.1	98.9	99.9	100.1

[1] n.d. = not determined.

LITHOLOGIC DESCRIPTION OF SAMPLES

1. Very coarse-grained (1–2 cm) calcitic marble exposed for 22.9 meters (m) transverse to strike. Sample consists of 10 cm cores from drill holes spaced at regular intervals across zone.
2. Selected specimen of very coarse, white calcitic marble similar to 1, above.
3. Chip sample of calcitic white marble same as sample 2, above. Exposed zone is 10.7 m wide transverse to strike.
4. Very coarse calcitic marble (1–2 cm) having flow banding vaguely outlined by fine-grained phlogopite and graphite. Sample is 13 short cores from holes spaced at regular intervals for 24 m across strike.
5. Selected specimen of light-gray to white, coarse-grained (0.5 to 1 cm) calcitic marble with accessory graphite in 1 mm flakes.
6. Sample is composite of short cores from holes spaced about 1.2 m apart across strike for 12 m of outcrop width. Rock is coarse-grained calcitic marble, same as sample 5, above.
7. Sample is composite of short cores from holes spaced about 1 m apart across strike for 5.5 m. Rock similar to sample 6, above.
8. Sample and rock as above from 11.6 m zone across strike.
9. Selected specimen of light-gray, graphitic dolomite with 1 to 5 mm grain size.
10. Selected specimen of light-gray, calcitic marble with layering outlined by dark, closely spaced dark-gray graphitic zones 5 to 10 mm wide.
11. Selected specimen of medium-grained (2 to 5 mm), medium gray, calcitic marble flecked with fine graphite and phlogopite flakes.
12. Selected specimen of dark gray, medium-grained scapolitic, graphitic and phlogopitic marble.
13. Selected specimen of white, coarse-grained (3 to 8 mm) marble flecked with 1 to 2 mm flakes of graphite and phlogopite.
14. Selected specimen of medium- and light-gray banded coarse-grained (2–5 mm) marble; contains graphite and phlogopite.

whereas tremolite is only about 14 percent CaO. Because tremolite is hydrous and diopside is not, the presence of significant water of crystallization in the analysis is an indication that the calc-silicate phase is probably tremolite rather than diopside, although the presence of diopside is not precluded. Samples 1 through 8 all contain water, and the calc-silicate mineral is assumed to be mainly tremolite. In order to further verify the noncarbonate mineral phases present in marble at sample sites 3 and 5, a 55-gram sample was dissolved in 15 percent HCL. The insoluble minerals were then identified microscopically, and identifications were verified by X-ray diffraction by Patricia Loferski of the U.S. Geological Survey. The most common minerals identified were tremolite, phlogopite, and graphite. Also present were a few grains of purple fluorite and a trace of pyrite. Therefore, calculations based on the suite—tremolite, dolomite, calcite—should give a close approximation of the $CaCO_3$ content for marble *A*.

One could also calculate $CaCO_3$ on the basis of the suite—quartz, dolomite, and calcite—but since quartz was not noted petrographically nor was it found in the one test for insoluble minerals in marble *A*, it was assumed to be essentially absent. However, in samples from marble unit *B*, after removing tremolite on the basis of available MgO, excess SiO_2 remains. In these samples, quartz is probably present. This is consistent with field observations of quartz in the calcitic marbles in unit *B*.

Table 2 lists the calculated $CaCO_3$ contents for samples 1 through 8; samples 9 through 14 were not calculated because they are too impure for high-calcium limestone. Note that after determining the calcite from CaO that remained after satisfying the formula for tremolite and dolomite in order to consume

TABLE 2.—*Calculated maximum and minimum* $CaCO_3$ *content for marble units A and B based on the mineral suite—tremolite, dolomite, quartz, and calcite*

Conversion factors for determining mineral content percentages from chemical analyses:

Calcite = 1.78 × CaO
Dolomite = 4.6 × MgO
Tremolite = 1.69 × SiO_2
4.05 × MgO
7.23 × CaO
Diopside = 1.8 × SiO_2
5.4 × MgO
3.86 × CaO

Note: These determinations are limited, of course, by availability of other oxides to satisfy the mineral formula.

Factors used to determine oxide contained in known percentage of mineral:

$$CO_2 = \frac{\text{percent calcite}}{2.27} \qquad CO_2 = \frac{\text{percent dolomite}}{2.09} \qquad CaCO_3 = \frac{\text{percent dolomite}}{1.84} \qquad CaO = \frac{\text{percent dolomite}}{3.28}$$

Sample No.	Calculated mineral percentage				Total $CaCO_3$ in calcite and dolomite[3]	Deficient or surplus oxides, in percent
	Tremolite	Quartz	Dolomite	Calcite		
[1]1	1.67	0	2.16	97.0	98.2	0.9 CO_2 deficiency
[2]1	1.67	0	2.16	95.0	96.2	1.1 CaO surplus
[1]2	.7	0	1.7	94.5	95.4	1.2 CO_2 surplus
[2]2	.7	0	1.7	97.2	98.1	0.9 CaO deficiency
[1]3	.68	0	3.22	96.0	97.7	1.0 CO_2 deficiency
[2]3	.68	0	3.22	93.7	95.4	1.7 CaO surplus
[1]4	1.5	0	6.1	95.1	98.4	2.2 CO_2 deficiency
[2]4	1.5	0	6.1	90.1	93.4	3.0 CaO surplus
[1]5	3.72	0	.9	92.9	93.4	1.2 CO_2 surplus
[2]5	3.72	0	.9	95.6	96.1	1.7 CaO deficiency
[1]6	3.28	1.9	0	97.5	97.5	0.5 CO_2 surplus
[2]6	3.28	1.9	0	96.2	96.2	0.7 CaO surplus
[1]7	6.1	.5	0	98.4	98.4	4.0 CO_2 deficiency
[2]7	6.1	.5	0	89.2	89.2	5.2 CaO surplus
[1]8	4.9	2.1	0	95.0	95.0	2.4 CO_2 deficiency
[2]8	4.9	2.1	0	89.4	89.4	3.2 CaO surplus

[1] Calcite calculated on basis of CaO available after removing CaO required to form tremolite and dolomite from available SiO_2 and MgO.

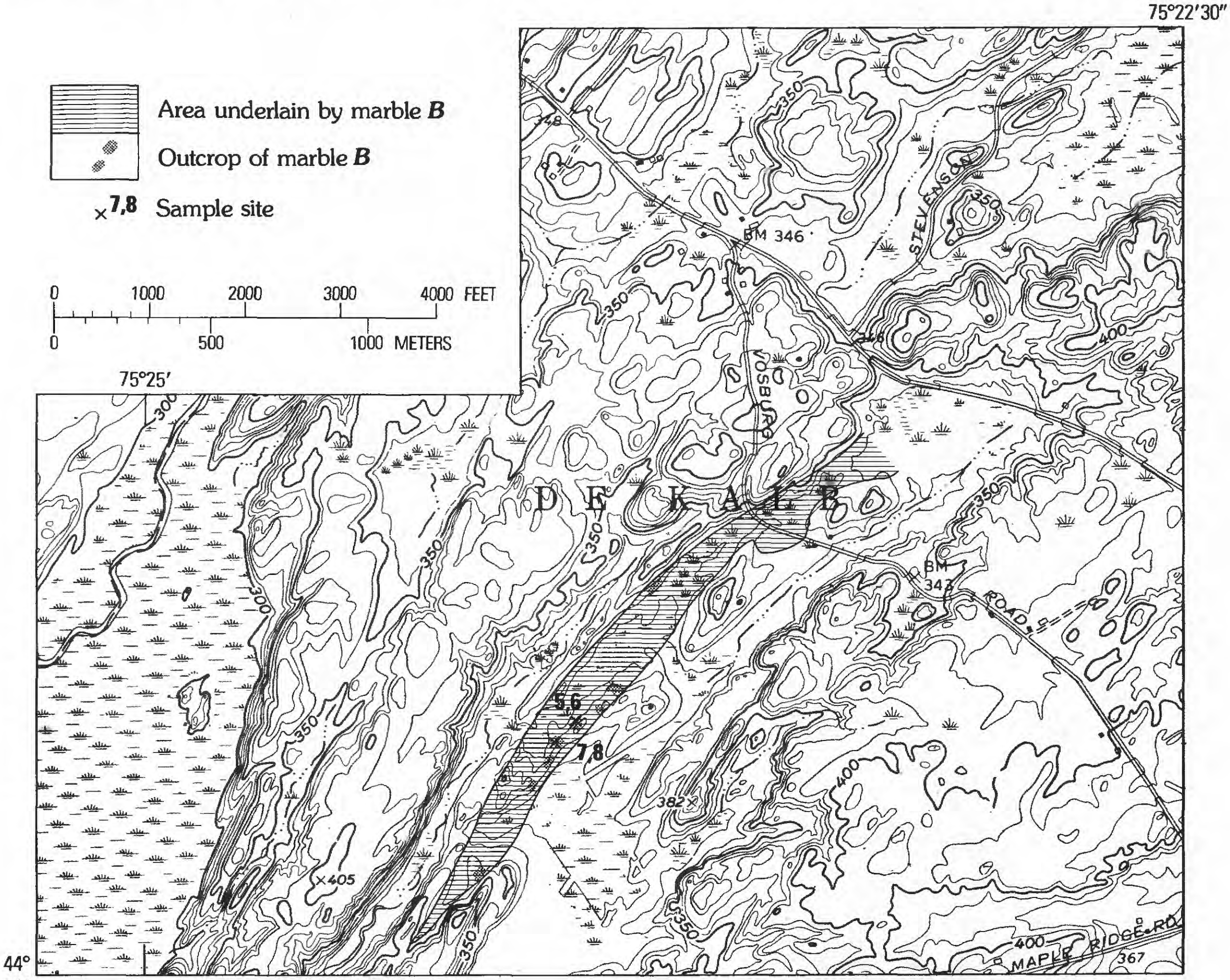
[2] Calcite calculated on basis of CO_2 available after removing CO_2 required to form dolomite from remaining MgO after tremolite.

[3] Maximum and minimum for each analysis.

SiO_2 and MgO, there is a deficiency of CO_2 in the analyses of some samples. Where a deficiency of CO_2 exists, $CaCO_3$ can be determined on the basis of CO_2 left after accounting for dolomite from MgO remaining after the percentage of tremolite is determined. Thus, two figures for total $CaCO_3$ are obtained which can be used as maximum and minimum values for $CaCO_3$ for each sample. Despite the irregularities inherent in this method of approximation, the minimum total $CaCO_3$ for most samples here is 95 percent or greater, which qualifies them as high-calcium limestones.

Marble, particularly from unit *A* and some from *B*, appears suitable for specialized applications requiring a high $CaCO_3$ content, and the low MgO, Fe_2O_3, and P_2O_5 greatly enhances their value for a variety of industrial uses, including glass manufacture. Samples of the high-calcium marble from unit *A* were also pulverized to determine whiteness and possible use as a mineral filler. Results were unfavorable because the finely ground material proved to be off-white owing to the minor quantity of graphite. Unless the graphite could be removed, the rock apparently is not suitable for use as a filler. It was also noticed that the coarsely crystalline character of the marble made grinding to a soft powder difficult because each particle is a tiny calcite cleavage rhomb.

The rock sampled from marble *B* at the northeast part of the area mapped in figure 5 (samples 5 through 8, table 1) is also a high-calcium rock, but represents a smaller surface area and therefore, is a smaller potential resource than marble *A*. Marble unit *B* sampled



Base from U.S. Geological Survey, Heuvelton, 1963

FIGURE 5.—Sample sites and outcrops in northeastern part of marble belt *B*.

elsewhere is more dolomitic, and typically the unit contains a great range of marble compositions from calcitic or dolomitic (sample 9) to quartz- and silicate-rich (sample 12). Marble *B*, represented by samples 10 and 11, might be chemically acceptable for some high-calcium uses such as in the manufacture of cement. However, the highly variable composition of marble in this belt stands against its use because of the difficulty of proving a large tonnage of uniform composition.

The marble in belt *C* is more uniform in composition than marble *B* and contains minor quantities of silicates. Samples 13 and 14 show it to be nearly pure, slightly magnesian marble.

CONCLUSIONS

A potentially large volume of high-calcium marble lies west of Beaver Creek. According to reconnaissance sampling, it contains greater, than 95 percent $CaCO_3$ and is low in MgO, Fe_2O_3, and P_2O_5, and thus is suitable as a raw material for a variety of chemical and metallurgical uses. The deposit is only 27.5 kms by road or railroad from port facilities on the St. Lawrence Seaway that can supply inexpensive transportation to markets along the Great Lakes, the St. Lawrence River, and possibly the east coast of North America.

Two other marble belts east of Beaver Creek also contain some high-calcium marble, but are more variable in composition and lithology than is the rock of the belt west of Beaver Creek.

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