RELATIONSHIP OF CARBONATE CEMENT TO LITHOLOGY AND VANADIUM-URANIUM DEPOSITS IN THE MORRISON FORMATION IN SOUTHWESTERN COLORADO

By N. L. Archbold

Trace Elements Investigations Report 513

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

IN REPLY REFER TO:

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

November 20, 1958

AEC - 87/9

Mr. Robert D. Nininger
Assistant Director for Exploration
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-513, "Relationship of carbonate cement to lithology and vanadium-uranium deposits in the Morrison formation in southwestern Colorado," by N. L. Archbold, July 1958.

We plan to submit this report for publication in Economic Geology.

Sincerely yours,

John H. Eric

for W. H. Bradley
Chief Geologist

Geology and Mineralogy

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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N. L. Archbold

July 1958

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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by N. L. Archbold

ABSTRACT

Carbonate content was determined for 888 samples from the Salt Wash member of the Morrison formation in the Slick Rock and Uravan mining districts in southwestern Colorado. The carbonate content of most samples was determined semiquantitatively by calculating the amount of calcite equivalent to the mass of carbon dioxide evolved when the samples were treated with 3 normal hydrochloric acid. The content of some samples was determined in the course of standard chemical assays and the content of others was visually estimated.

Samples were assigned to categories or "rock types" on the basis of gross lithology, vanadium-uranium content, degree of epigenetic alteration, and degree of oxidation through weathering. The average carbonate content was determined for each rock type, and the distribution of carbonate around oxidized and unoxidized ore was investigated.

Results indicate that sandstone in the uppermost (ore-bearing) part of the Salt Wash member contains 2.5 to 3.0 percent carbonate, whereas sandstone in the lower (generally barren) part of the Salt Wash member contains approximately 10 percent more carbonate. Altered mudstone in the Salt Wash member contains about 4 percent carbonate, or about 3 percent less than the unaltered mudstone.

Carbonate-rich zones in sandstone, adjacent to contacts with mudstone, may be of syngenetic or early diagenetic origin, whereas carbonate-rich zones associated with ore bodies may be genetically related to the ore deposits.

Where the sandstone has been subjected to weathering, the overall distribution of carbonate does not seem to have been greatly affected.

INTRODUCTION

Vanadium-uranium deposits in sandstone on the Colorado Plateau are now generally thought to have had an epigenetic origin, though there is no agreement as to the specific nature of the mineralizing process. Regardless of the nature of the epigenetic mineralizing process, it may have had an effect upon distribution of carbonate cement in the host sandstone, or the process itself may have been influenced by the original distribution of carbonate cement. The present study was undertaken to determine how carbonate cement is distributed in the Salt Wash member of the Morrison formation and if this distribution shows any relation to vanadium-uranium deposits in the Salt Wash.

This work was done by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

THE MORRISON FORMATION

The Morrison formation of Late Jurassic age is widely distributed in the western interior of the United States. Regional characteristics and differences have been described by Craig and others (1). This paper is concerned with areas in southwestern Colorado where the Morrison formation is divided into two members; the Brushy Basin member and the underlying Salt Wash member. The Brushy Basin member ranges from about 300 to 700 feet in thickness, and is composed of varicolored bentonitic mudstone with minor interbedded lenses of conglomerate and sandstone which are more abundant near the base of the member.

In the areas covered by this report, the Salt Wash member of the Morrison formation ranges from about 275 to 450 feet in thickness and is composed of mudstone with interbedded lenses of quartzose sandstone. The mudstone is dominantly reddish brown and the sandstone is light red to light gray or buff. Most of the carbonate within the sandstone occurs as cementing material.

The Salt Wash member can be divided roughly into three parts. At the top and bottom of the Salt Wash member, lenses of sandstone coalesce and form fairly continuous layers of sandstone which contain numerous thin layers of mudstone. The central part of the Salt Wash member is composed dominantly of mudstone containing scattered, unconnected lenses of sandstone. Contacts between the three parts of the Salt Wash member interfinger and are more evident when viewed on a broad scale. Most of the significant vanadium-uranium deposits in the Morrison formation occur in the top sandstone layer of the Salt Wash member, which is commonly referred to as the "ore-bearing sandstone."

In the vicinity of vanadium-uranium deposits, the normally light-red to red-brown sandstone and mudstone are light gray to brown and gray green to yellow brown, respectively. The light-gray, brown, and gray-green colors resulted primarily from epigenetic bleaching of originally red sediments (3), though locally, where sandstone contains abundant carbonaceous material, the bleaching may have been the result of diagenetic as well as epigenetic processes. In this study, all rocks which are shades of gray, green, or brown are considered to have been epigenetically bleached. In the subsequent discussion, these bleached rocks will be referred to as "altered" rocks. The unbleached rocks, which are shades of red, will be referred to as "unaltered."

Partial oxidation of the rocks has occurred where the Salt Wash member has been exposed to atmospheric conditions. This partial oxidation is indicated by the formation of limonite from pyrite, the formation of secondary uranium minerals, and the destruction of small amounts of carbonaceous material. In this paper, the term "oxidized" will be used to indicate rocks which, after their formation, have been subjected to the oxidizing environment of the atmosphere, but have not necessarily been oxidized so completely that all elements are in their highest valence state. According to this usage, rocks classed as oxidized may show a wide range in actual, overall oxidation state, as the term "oxidized" applies only to the epigenetic history of the rock, not to the overall oxidation state.

It is necessary to distinguish between altered, unaltered, oxidized, and unoxidized samples, because alteration and oxidation, as here defined, may have caused significant changes in the distribution of carbonate cement. Color is a good indication of the relative degree of alteration and oxidation. Unaltered rocks are light red to brownish red, and because their components were originally deposited in a high state of oxidation, they undergo no color change when subjected to the oxidizing conditions of weathering. Despite the fact that unaltered rocks may have undergone no appreciable overall oxidation during weathering, the weathered and unweathered varieties will be referred to as "oxidized" and "unoxidized" to maintain a consistent terminology. Altered unoxidized rocks are light gray to gray green. Upon oxidation, altered mudstone may become yellow brown, but more commonly it maintains a gray-green color. Altered sandstone, when oxidized, is yellow brown and commonly has a brown speckling. Unoxidized vanadium-uranium minerals are black; oxidized minerals are shades of yellow, red, or orange.

The rocks of the Salt Wash member can be divided into categories on the basis of particle size, vanadium-uranium content, alteration, and oxidation. These categories will be called the "principal rock types" of the Salt Wash member. For clarification, these rock types and their characteristic colors are listed in table 1.

METHOD OF INVESTIGATION

Samples were collected from mine workings and diamond-drill cores so that their spatial position relative to lithologic contacts and mineralized zones was known. Samples collected from outcrops or associated with oxidized ore minerals were considered to be oxidized, whereas samples collected from deep drill holes, well below the present water table, or samples associated with unoxidized ore-minerals, were considered to be unoxidized.

Quantitative data on the carbonate content of each sample were obtained by one of three methods. Chemical assays of 162 samples were made for vanadium oxide, uranium oxide, and calcium carbonate. A rapid, semiquantitative method of analysis was adapted and used by the author to obtain data on 467 samples. Finally, estimates were made of the carbonate content in 259 samples. Each analytical method is described in a following section.

Table 1.--Principal rock types in the Salt Wash member of the Morrison formation and their characteristic colors

Rock type	Unoxidized	Oxidized
Mineralized sandstone _/	Gray to black	Gray to black with various amounts of yellow, red, or green
Barren sandstone		
Unaltered	Light red to brownish red	Light red to brownish red
Altered	Light gray	Yellow brown to buff. Commonly with brown speckling
Mudstone		
Unaltered	Brownish red	Brownish red
Altered	Gray green	Gray green with minor yellow brown

_/ All mineralized sandstone is altered

Source of samples

Most of the samples for this study are from the Disappointment Valley area of the Slick Rock mining district, San Miguel County, Colo. (figs. 1 and 2), where samples were collected from mines in oxidized ore deposits and from drill cores in both oxidized and unoxidized rocks. In the Uravan mining district, Montrose County, Colo., 132 unoxidized samples were collected from the Virgin and Golden Cycle mines (fig. 1). Table 2 shows the number of samples collected from each locality and rock type, as well as the number treated by each of the three analytical methods.

Methods of analysis for carbonate

A rapid semiquantitative method for carbonate analysis was used to analyze 467 samples. The method, adapted from that described by Scott and Jewell (2), consisted of calculating the mass of carbon dioxide liberated when a rock sample of known weight was treated with hydrochloric acid. Analysis was carried out in three steps: first, a 100 ml. beaker containing 10 ml. of 3 normal hydrochloric acid was weighed; then, a weighed sample of crushed rock (3 to 5 grams) was placed in the acid, and the resulting reaction was allowed to proceed until all effervescence stopped; finally, the beaker containing the acid solution and rock residue was reweighed and the mass of evolved carbon dioxide was calculated. The mass of carbon dioxide was then converted to an equivalent mass of calcium carbonate, and the total percentage of carbonate (calculated as calcium carbonate) in the rock sample was determined.

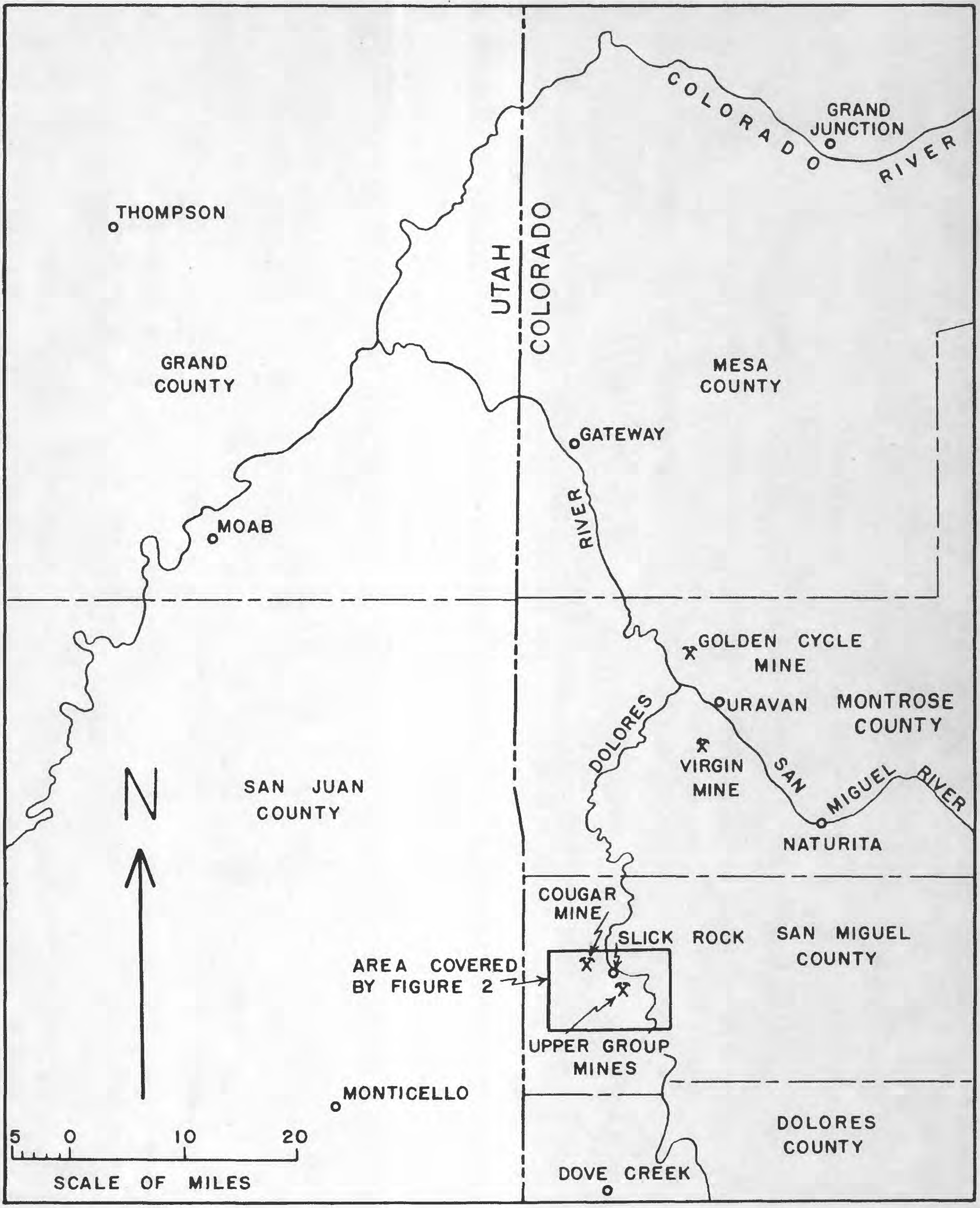

FIGURE 1. — INDEX MAP OF PART OF COLORADO PLATEAU SHOWING LOCALITIES REFERRED TO IN TEXT.

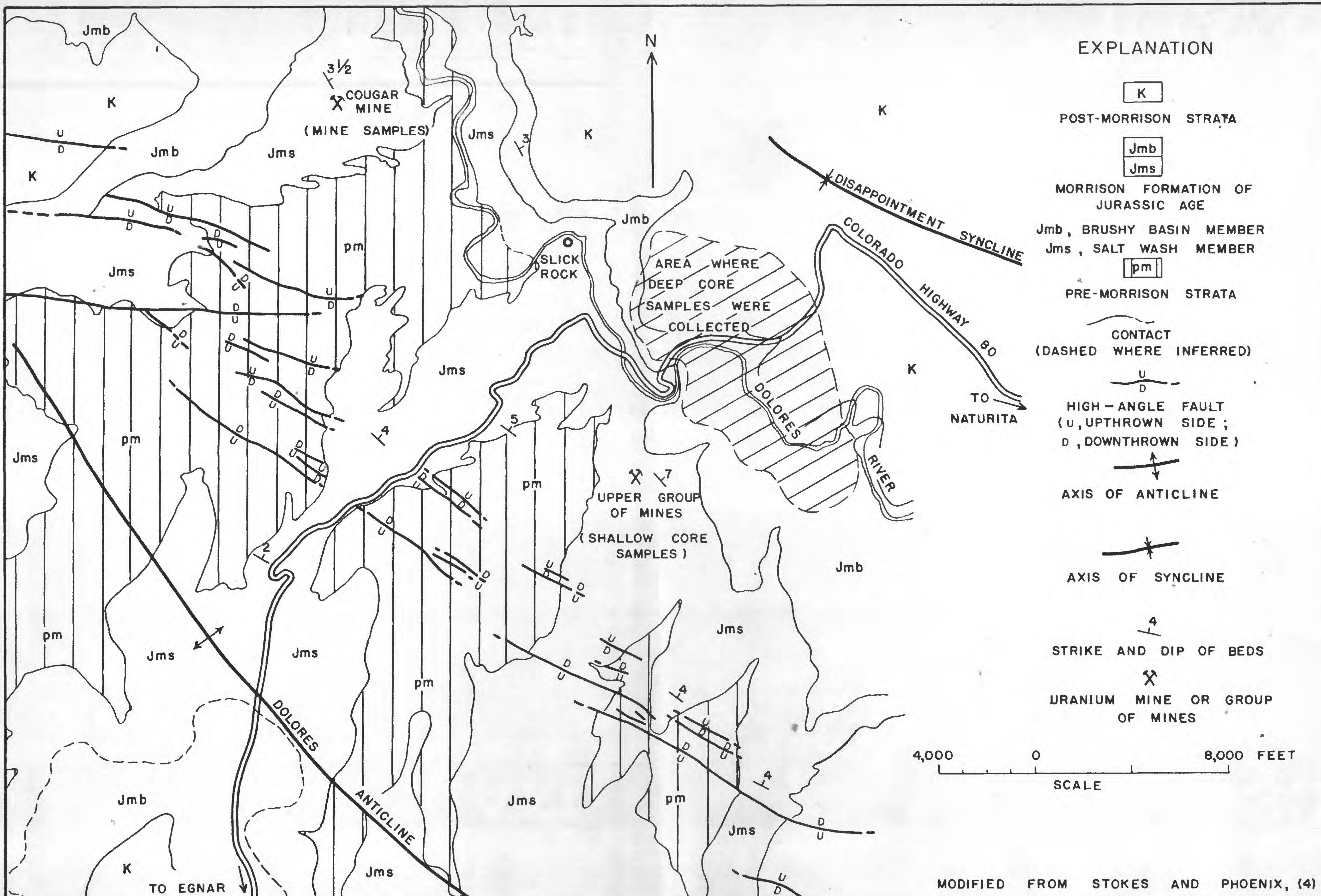

FIGURE 2. — GENERALIZED GEOLOGIC MAP OF DISAPPOINTMENT VALLEY AREA SHOWING SAMPLE LOCALITIES.

Table 2. Number of samples collected, showing sample locality, type of sample, and method of analysis.

Sample locality	Rock type	Number of samples		Method of carbonate determination		
		Unoxidized	Oxidized	Rapid method	Chemical assay 1/	Estimation
Slick Rock district						
Disappointment Valley area	Altered barren sandstone	238	--	238	--	--
	Unaltered barren sandstone	47	--	47	--	--
	Altered mudstone	47	--	47	--	--
	Unaltered mudstone	47	--	47	--	--
	Mineralized sandstone	58	--	--	58	--
Upper Group mines	Mineralized sandstone	--	104	--	104	--
Cougar mine	Mineralized sandstone	--	33	16	--	17
	Altered barren sandstone	--	175	72	--	103
	Altered mudstone	--	7	--	--	7
Uravan district						
Golden Cycle mine	Mineralized sandstone	12	--	--	--	12
	Altered barren sandstone	44	--	--	--	44
Virgin mine	Mineralized sandstone	32	--	--	--	32
	Altered barren sandstone	44	--	--	--	44
	Totals	569	319	467	162	259

Total number of samples = 888

1/ Assays made by C. Angelo, G. Boyes, Jr., R. Dufour, M. Finch, S. Furman, R. Havens, C. Horr, H. Lipp, E. Mallory, J. Meadows, T. Miller, J. Patton, L. Rader, D. Shafer, J. Schuch, D. Skinner, D. Stockwell, J. Wahlberg, and J. Wilson, U. S. Geological Survey.

Inaccuracies may have resulted from 1) evaporation of acid or loss due to splattering, 2) absorption of carbon dioxide by the acid solution, 3) materials in the rock sample, other than calcium carbonate, which may have reacted with acid, and 4) carbonates which did not react with the acid solution. The first two sources of error were reduced by rapid work, careful addition of the crushed rock to the acid, and use of a volume of acid not too much in excess of that needed to react completely with the sample. All carbonate was calculated as calcite, although locally carbonates in the Salt Wash member are dolomitic, sideritic, or ankeritic. Errors in absolute percentage of carbonate have probably resulted, but these errors are believed to be small and the effect on relative amounts of carbonate in samples from the same locality is probably negligible unless amounts of magnesium, iron, and manganese have a wide range in different rock types in the same area. Carbonates that contain appreciable amounts of iron, manganese, or magnesium react slowly with the acid and loss of weight through evaporation causes errors so large that the method cannot be used. All samples from the Disappointment Valley area reacted quite readily with the acid and the carbonate is probably largely calcite. Table 3 shows the accuracy of this method when used on standards prepared by mixing known amounts of powdered calcite and acid-washed sand. Where natural, rather than artificial, samples are used the errors are no doubt slightly larger, but the method seems adequate for semiquantitative work and has the advantage that analyses can be made quite cheaply and rapidly.

Table 3.--Carbonate content determined by using rapid analytical method on prepared standards

Actual percent carbonate (as $CaCO_3$)	Percent carbonate by rapid analytical method
0.0	0.2
0.0	0.5
1.1	1.2
2.3	2.3
4.6	4.6
5.8	5.9
7.4	7.6
8.4	8.4
8.6	8.1
10.8	9.7
14.5	14.0
15.1	14.1
21.1	20.2
33.9	34.6
100.0	102.0
100.0	102.9

Standard chemical assays for uranium oxide, vanadium oxide, and calcium carbonate were made by analysts of the U. S. Geological Survey. An acetic acid leaching process was used to determine percentages of calcium carbonate. Where it has been possible to compare these determinations with those made using the rapid analytical method, the two are in close agreement.

Carbonate contents of some samples from the Cougar mine (Slick Rock district) and all samples from the Uravan district were estimated. Samples from the Golden Cycle and Virgin mines in the Uravan district reacted slowly with the acid solution and for this reason the rapid analytical method could not be used. Estimates were made by treating the samples with dilute hydrochloric acid, then classifying the samples as containing none, trace, sparse, moderate, or abundant carbonate by the degree of effervescence. To evaluate the carbonate percentages in each of these categories, the estimated content for some samples was compared with the content determined using the rapid analytical method. Those samples estimated to contain a "trace" of carbonate contained 0.5 percent or less, "sparse" from 0.5 to 1.5 percent, "moderate" from 1.5 to 5.0 percent, and "abundant" more than 5.0 percent carbonate. The percentages given apply only to samples from the Slick Rock district. Actual percentages were not determined for samples from the Uravan district because they reacted too slowly with the acid, probably because they contain appreciable amounts of magnesium.

For the purposes of comparing groups of analyses, the geometric mean has been used as the measure of central tendency because this measure minimizes the effect of a few abnormally low or high individual determinations and gives a truer average for each group.

RESULTS

Carbonate content of principal rock types of the Salt Wash member

Figures 3 and 4 show histograms of carbonate content for each of the principal unoxidized rock types. From the geometric mean values in figures 3 and 4, three conclusions are drawn: 1) all types of unoxidized sandstone are similar in average carbonate content, 2) unoxidized mudstone contains more carbonate than unoxidized sandstone, and 3) altered mudstone contains slightly less carbonate than unaltered mudstone, though both show a wide range in carbonate content. Limy nodules are locally abundant in gray-green mudstone and may be the cause for the bimodal histogram shown in figure 3B.

Mean carbonate percentages for all types of oxidized rocks have not been determined although oxidized and unoxidized mineralized sandstone have been compared (fig. 4). The mean values for carbonate in oxidized and unoxidized mineralized sandstone, 3.0 percent and 2.6 percent respectively, are fairly close, though there is a difference in the two distributions. Carbonate in oxidized mineralized sandstone has a unimodal distribution, whereas in unoxidized mineralized sandstone it has a bimodal distribution. The reason for this difference in distribution is not apparent; possibly the bimodal distribution resulted from re-

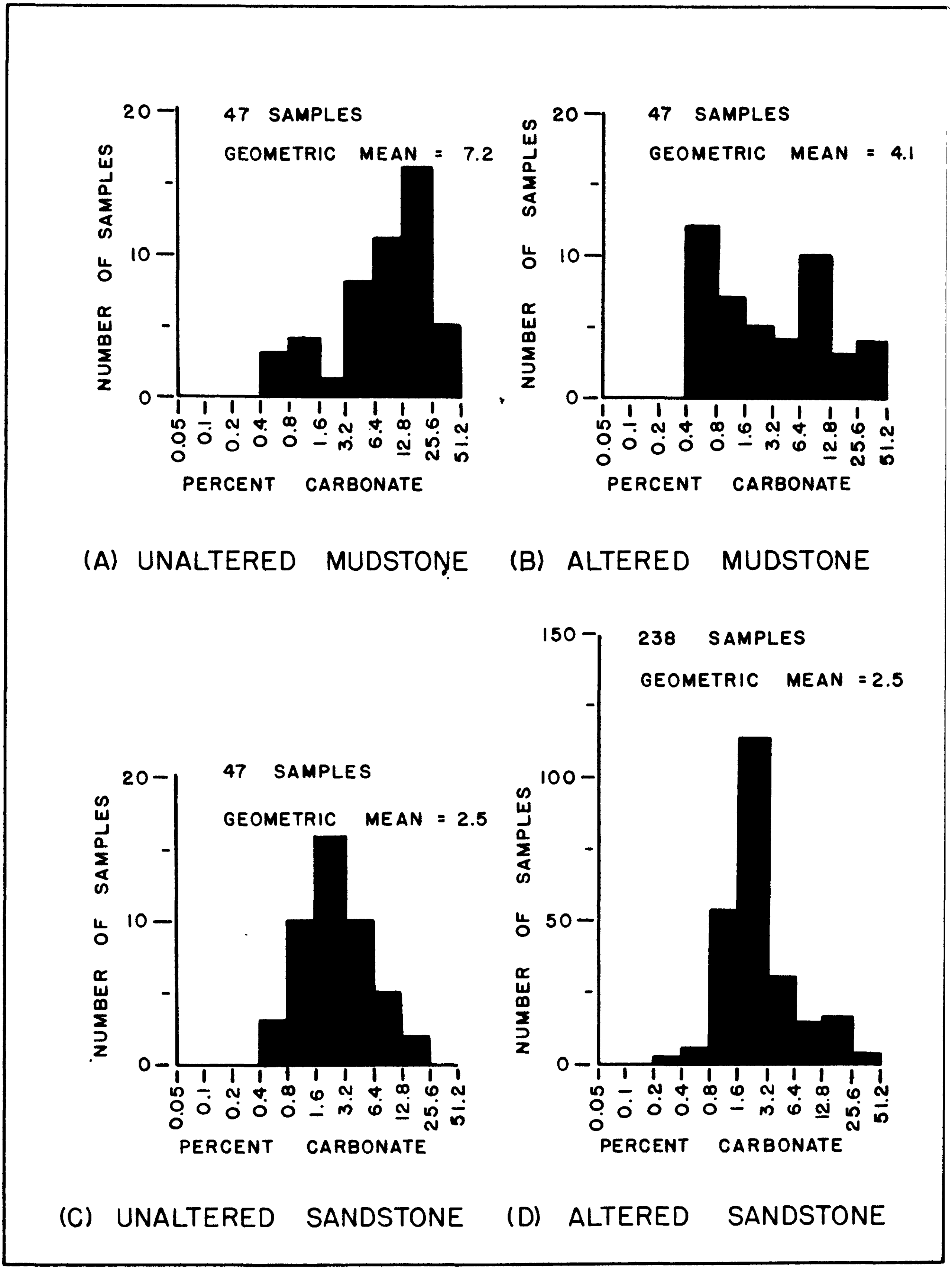

FIGURE 3.— COMPARISON OF CARBONATE CONTENT IN BARREN UNOXIDIZED ROCKS OF THE SALT WASH MEMBER OF THE MORRISON FORMATION.

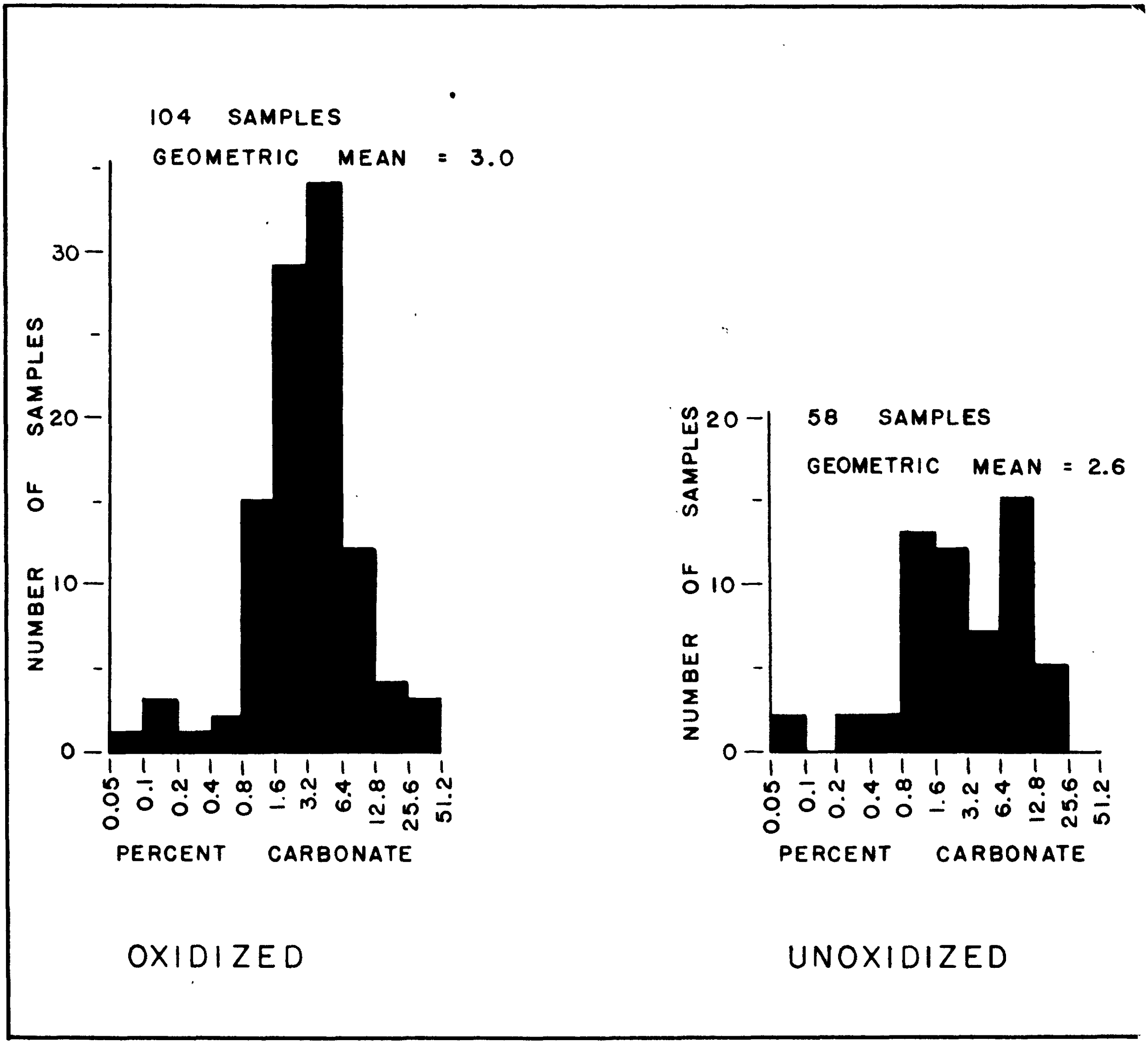

FIGURE 4 — CARBONATE CONTENT IN MINERALIZED SANDSTONE OF THE SALT WASH MEMBER OF THE MORRISON FORMATION.

of the bimodal distribution may have resulted from changes during oxidation.

Estimates of carbonate content in sandstone of the lower Salt Wash indicate that the lower sandstone (generally barren) contains appreciably more carbonate than the upper (ore-bearing) sandstone. This is in agreement with the work of Craig and others (1, p. 147) who report an average of 13 percent carbonate cement for sandstone of the Salt Wash as a whole.

Carbonate distribution at lithologic contacts

The carbonate content of oxidized and unoxidized sandstone is generally greatest adjacent to contacts with mudstone (fig. 5) where, according to data obtained by Robert A. Cadigan and David A. Phoenix (oral communications, 1955), sorting and permeability in the sandstone are at a minimum.

Samples were taken on either side of contacts between brownish red (unaltered) and gray-green (altered) mudstone. At 10 of the 17 contacts sampled, the carbonate content was significantly less on the gray-green (altered) side of the contact (table 4). At 2 contacts, there was essentially no difference in the amount of carbonate on either side, and at the remaining 5 contacts, the carbonate concentration was greater on the gray-green side.

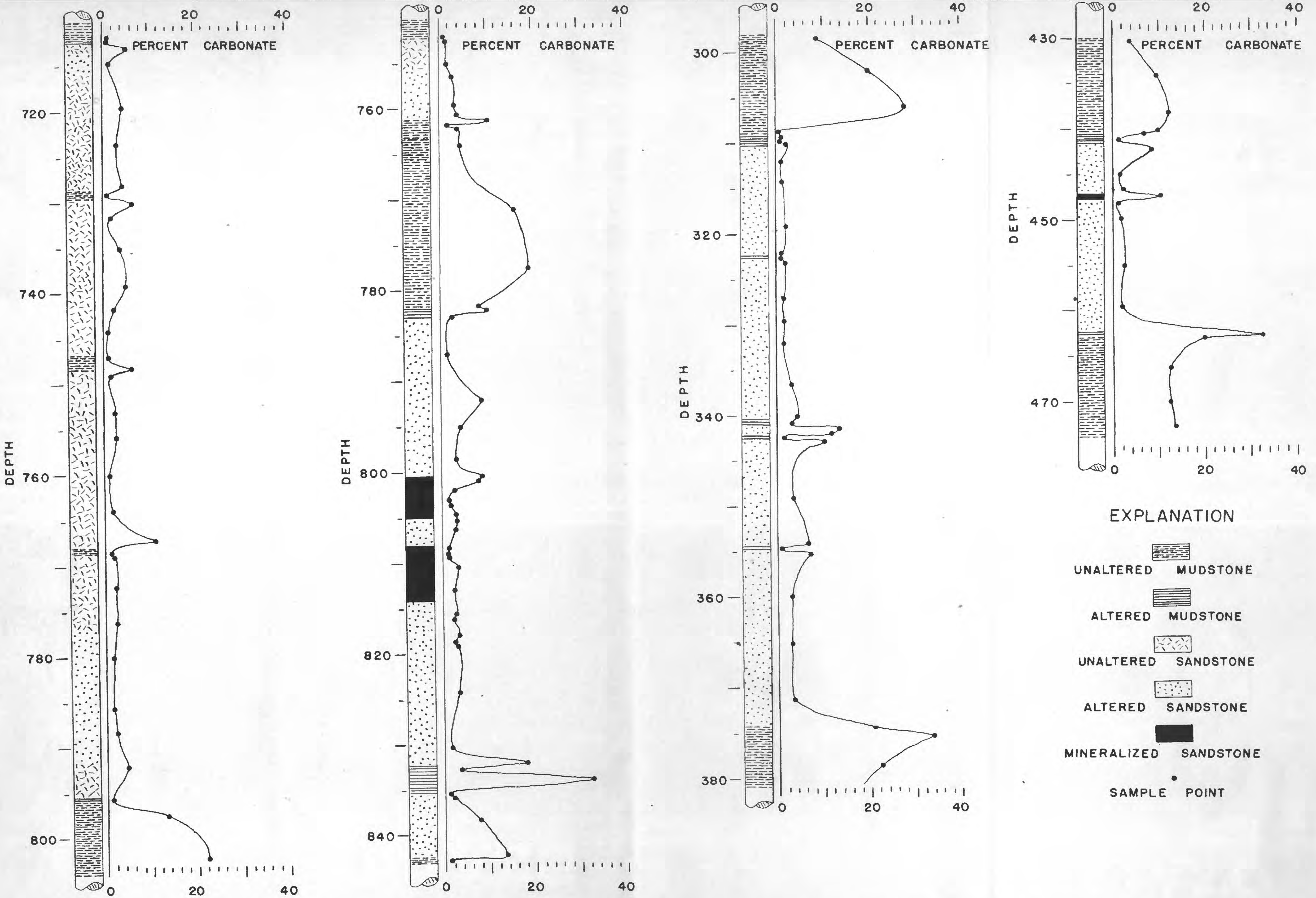

FIGURE 5.— DISTRIBUTION OF CARBONATE IN UNOXIDIZED DRILL CORES THROUGH THE TOP PART OF THE SALT WASH MEMBER OF THE MORRISON FORMATION.

Carbonate and vanadium-uranium content

In the Disappointment Valley area, no correlation exists between the carbonate content and the vanadium or uranium content of mineralized samples. This lack of correlation is apparent in both oxidized and unoxidized sandstone (figs. 6, 7, 8, and 9).

Table 4.--Comparison of carbonate content on either side of alteration contacts in mudstone

Percent carbonate in altered mudstone	Percent carbonate in unaltered mudstone	Vertical distance separating samples (in feet)
0.4	0.9	0.2
0.8	12.4	2.1
1.1	28.5	3.3
37.0	20.9	0.5
3.1	10.2	0.5
2.2	19.1	1.0
0.7	12.5	0.3
0.7	7.0	1.1
10.5	7.8	0.2
9.3	6.3	0.3
3.8	5.6	0.3
6.7	5.1	0.1
3.5	5.6	0.3
11.4	16.8	0.4
47.1	16.3	0.4
13.6	13.2	0.3
0.0	0.0	0.5

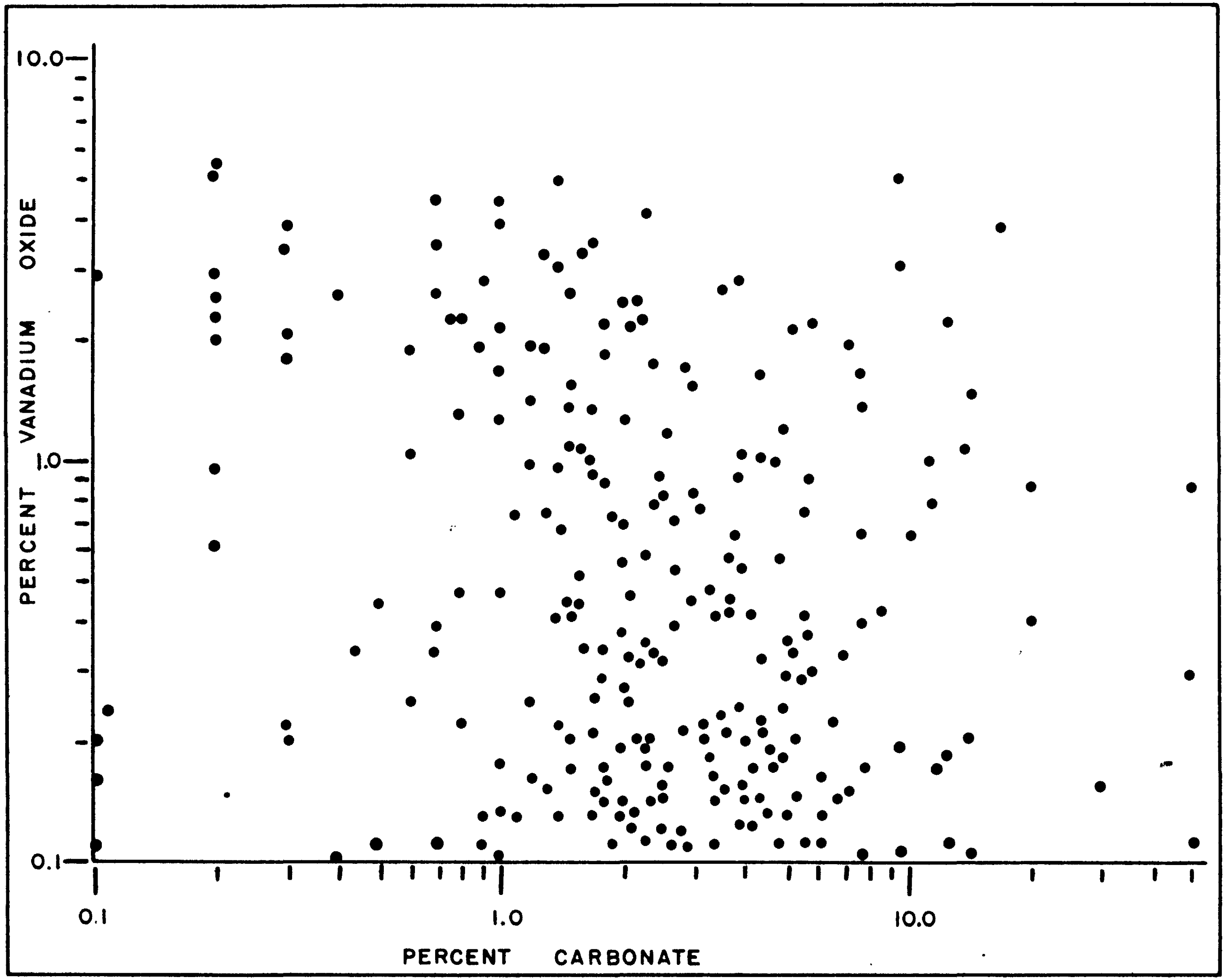

FIGURE 6. — CARBONATE VERSUS VANADIUM OXIDE IN SAMPLES OF OXIDIZED SANDSTONE, UPPER GROUP OF MINES, SAN MIGUEL COUNTY, COLO.

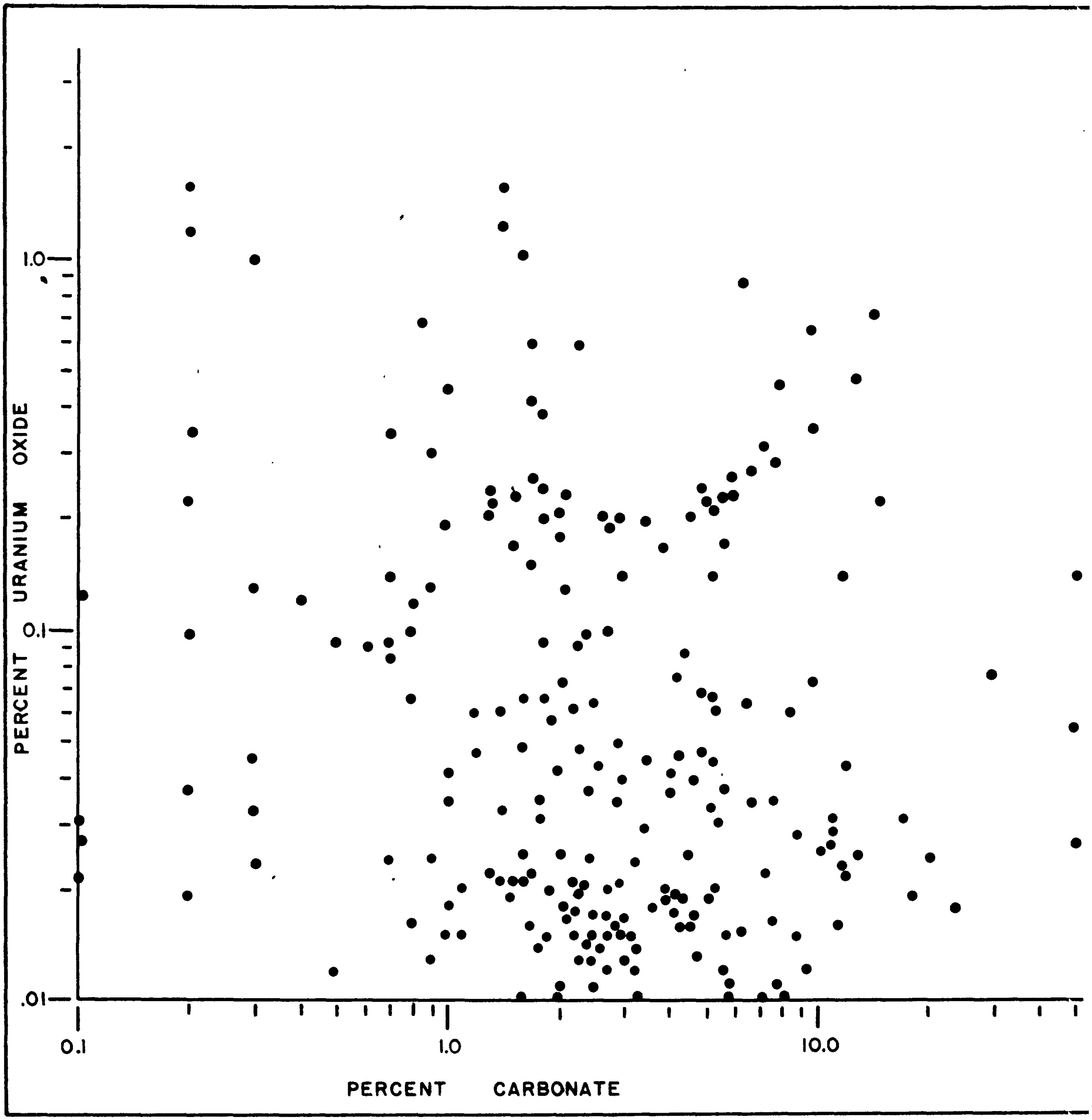

FIGURE 7 — CARBONATE VERSUS URANIUM OXIDE IN SAMPLES OF OXIDIZED SANDSTONE, UPPER GROUP OF MINES, SAN MIGUEL COUNTY, COLO.

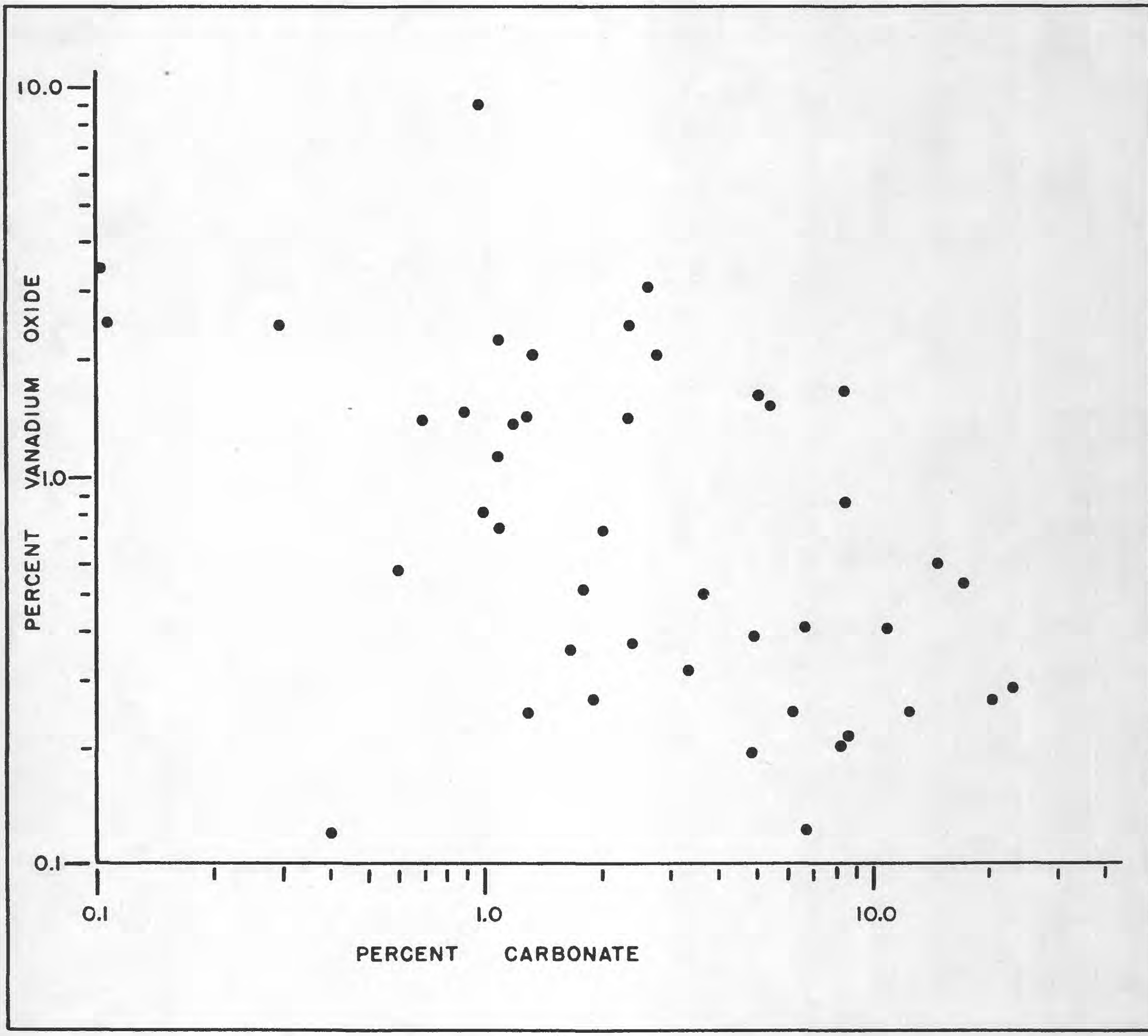

FIGURE 8.— CARBONATE VERSUS VANADIUM OXIDE IN SAMPLES OF UNOXIDIZED SANDSTONE, DISAPPOINTMENT VALLEY AREA, SAN MIGUEL COUNTY, COLO.

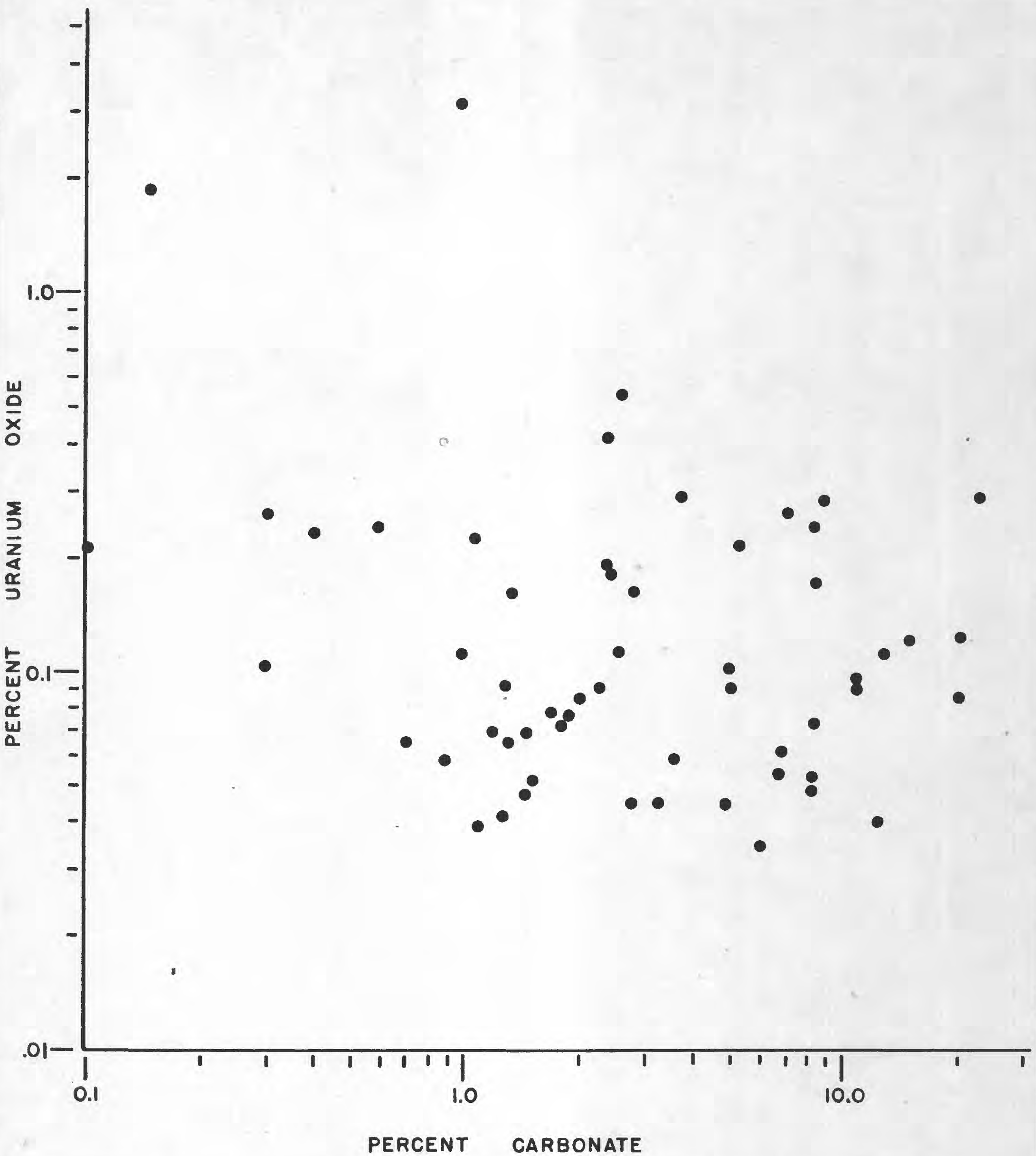

FIGURE 9.— CARBONATE VERSUS URANIUM OXIDE IN SAMPLES OF UNOXIDIZED SANDSTONE, DISAPPOINTMENT VALLEY AREA, SAN MIGUEL COUNTY, COLO.

Carbonate distribution relative to mineralized sandstone

Ore bodies in sandstone of the Salt Wash member occur in two forms: irregular tabular or lenticular masses that are flat lying but which may pinch and swell in short distances, locally cutting across the bedding; and elongate bodies called "rolls" which have curved cross sections and cut sharply across bedding. An ore deposit may be composed mainly of one type of ore body, but most deposits contain both types.

Samples from mines indicate that higher than average amounts of carbonate (more than 3 percent) occur in sandstone in zones close to and roughly parallel to both types of ore bodies in both oxidized and unoxidized ore deposits. Carbonate-rich layers occur above and below tabular or lenticular ore bodies; these layers are up to several feet thick and may be in contact with the ore or separated from it by several feet of barren sandstone containing average amounts of carbonate (figs. 10 and 12). The ore contains near-average amounts of carbonate. Carbonate-rich zones are also found adjacent to and roughly parallel to roll-type ore bodies (figs. 11 and 12).

Carbonate-rich zones are also associated with mineralized sandstone in unoxidized drill cores (fig. 5).

SUMMARY AND CONCLUSIONS

Sandstone from the top (ore-bearing) unit of the Salt Wash member of the Morrison formation contains an average of 2.5 to 3.0 percent carbonate regardless of whether or not it has been epigenetically altered, mineralized, or weathered (oxidized). The lower (generally barren) sandstone lenses of the Salt Wash member contain several times

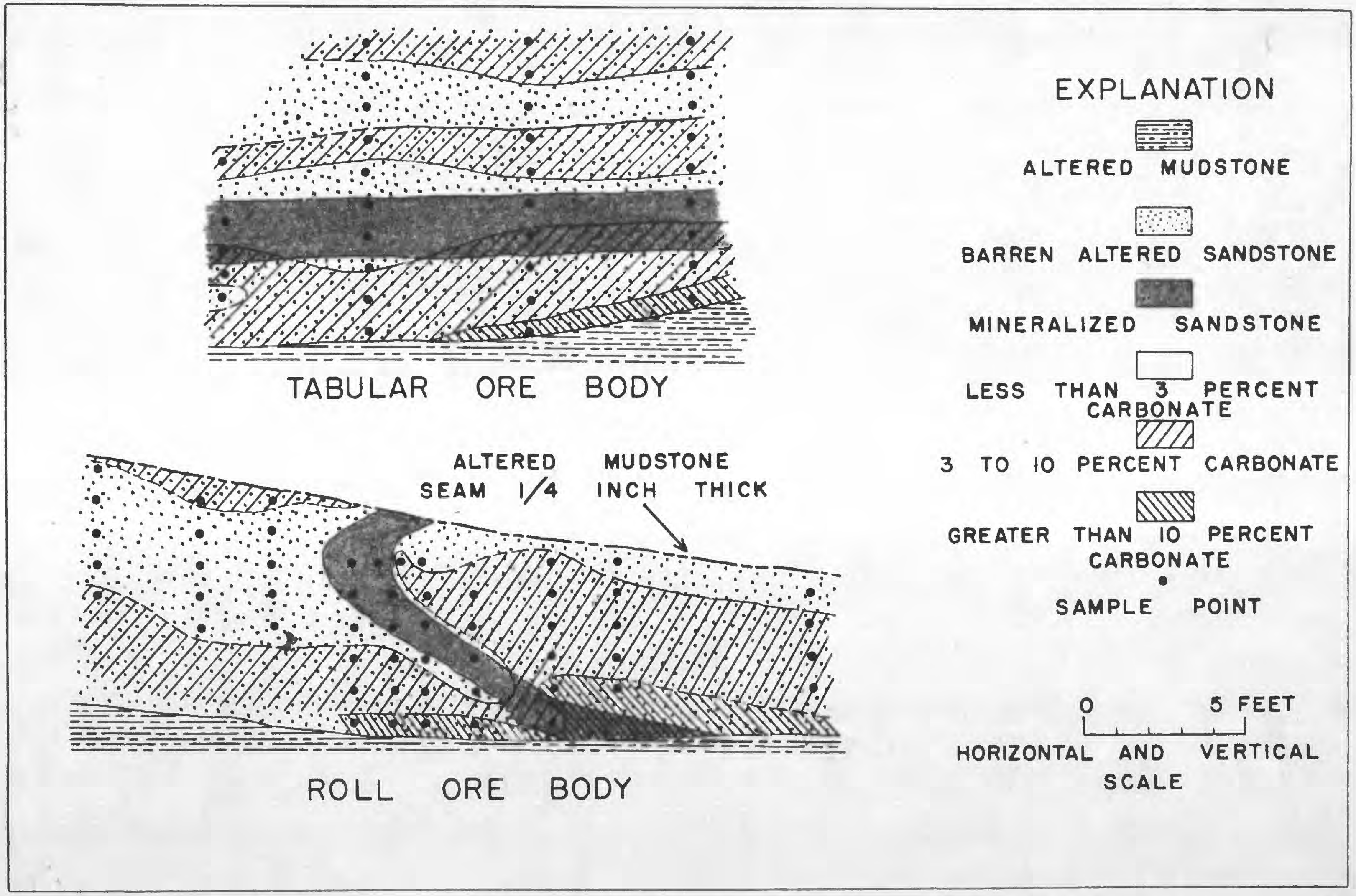

FIGURE 10. — DISTRIBUTION OF CARBONATE IN FACES OF OXIDIZED ORE, COUGAR MINE, SAN MIGUEL COUNTY, COLO.

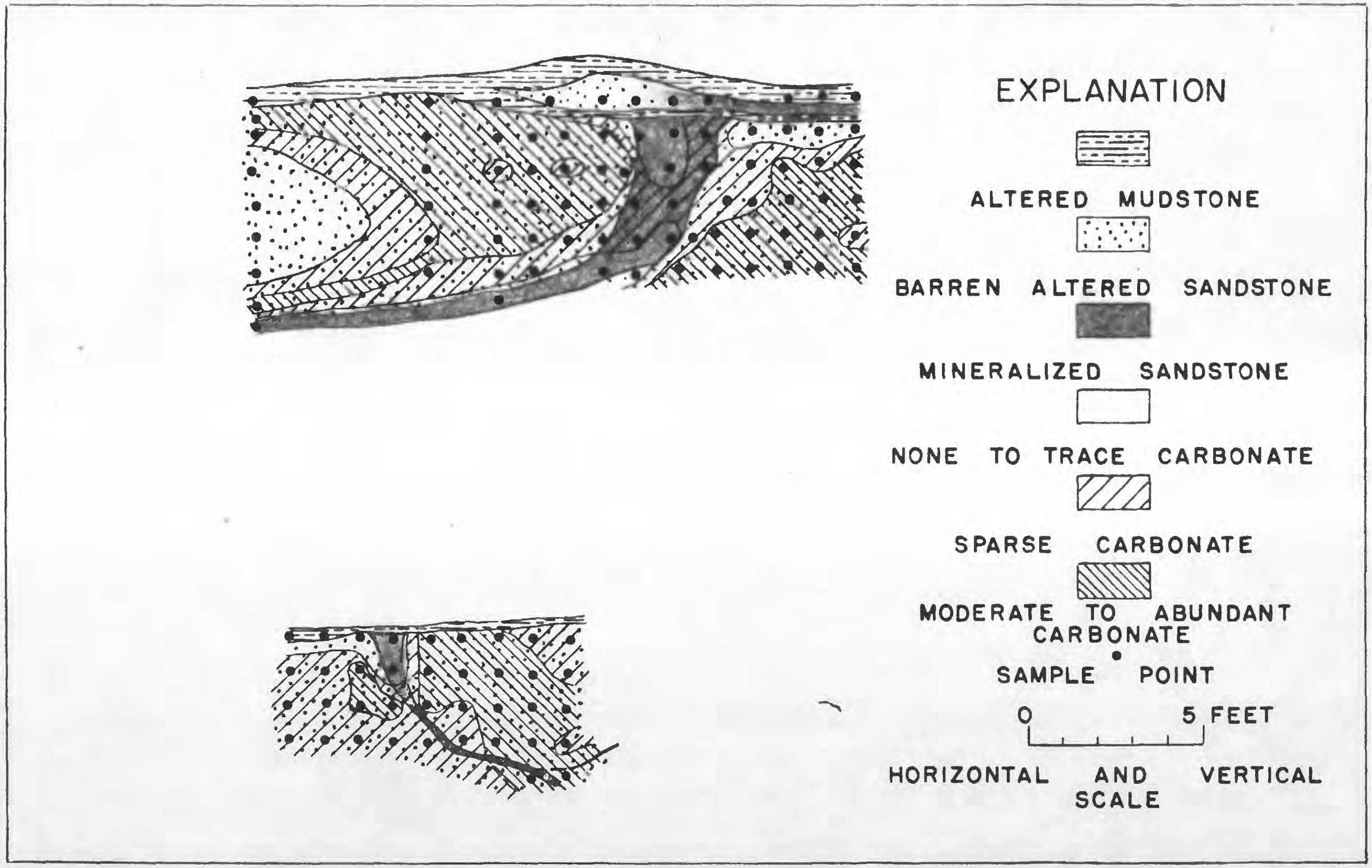

FIGURE 11. — DISTRIBUTION OF CARBONATE AROUND OXIDIZED ROLL ORE BODIES, COUGAR MINE, SAN MIGUEL COUNTY, COLO. (BASED ON ESTIMATES OF CARBONATE CONTENT).

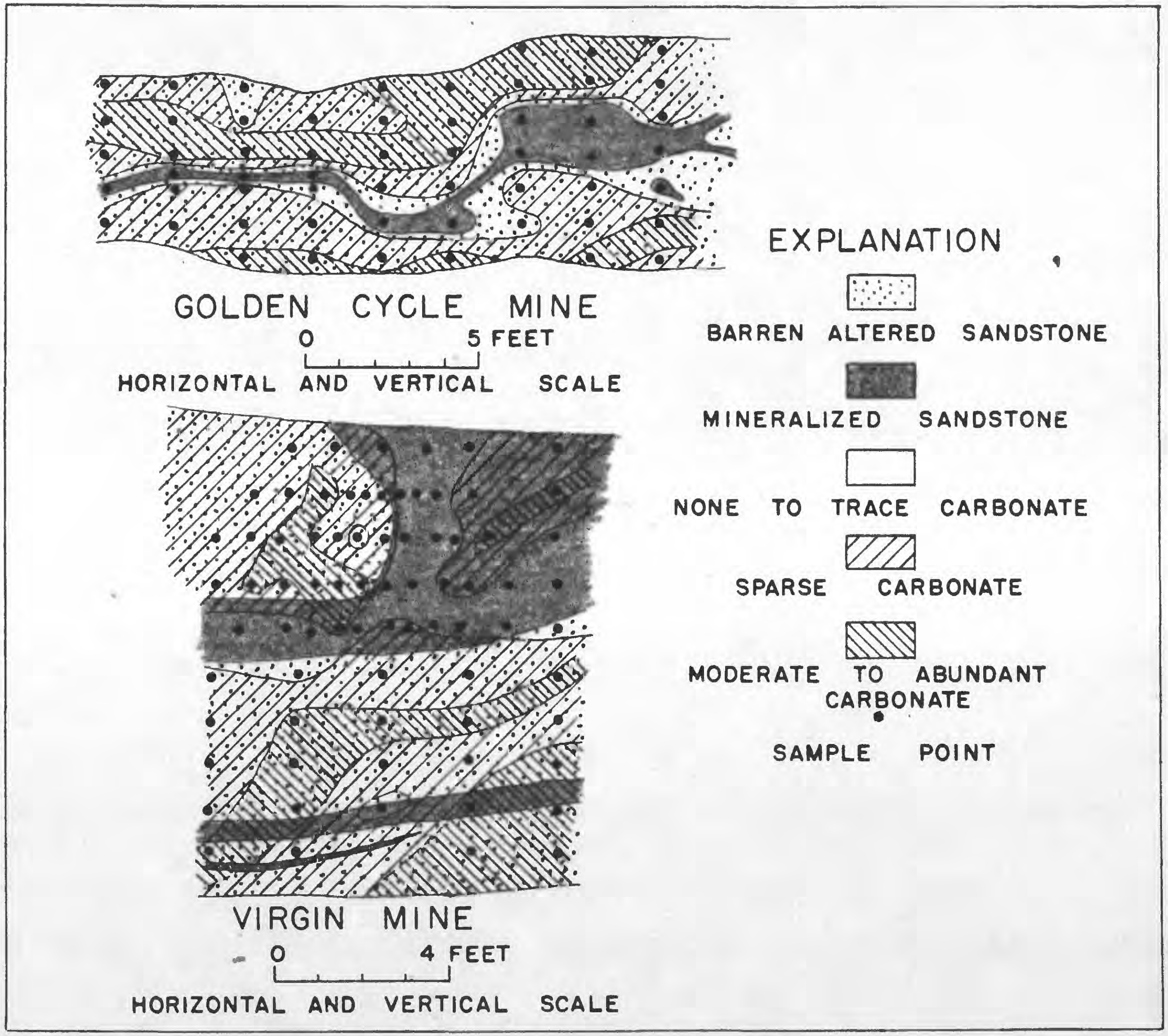

FIGURE 12.— DISTRIBUTION OF CARBONATE AROUND UNOXIDIZED ORE BODIES, URAVAN DISTRICT, MONTROSE COUNTY, COLO. (BASED ON ESTIMATES OF CARBONATE CONTENT).

more carbonate than those of the upper sandstone. It appears that the ore-bearing sandstone originally contained less carbonate cement.

Altered mudstone contains slightly less carbonate than unaltered mudstone and the process of mudstone alteration probably involved some leaching of carbonate. On the other hand, altered and unaltered sandstone have about the same amount of carbonate, and possibly the mudstone and sandstone were altered by different agents.

Carbonate-rich zones adjacent to contacts with mudstone are probably syngenetic or early diagenetic features, whereas carbonate-rich zones are closely associated in space with ore bodies and may be genetically related to ore deposits.

Where the ore-bearing sandstone has been subjected to weathering and associated oxidation, the average carbon content has apparently not been greatly changed nor has carbonate been appreciably redistributed.

Should further work show that certain carbonate-rich zones or types of carbonate are genetically associated with ore bodies these zones of carbonate might be useful as ore guides.

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