Argentian Cryptomelane and Bromargyrite in Volcanic Rocks near Silver Cliff, Colorado

GEOLOGICAL SURVEY BULLETIN 1382-C

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By FRED A. HILDEBRAND *and* ELWIN L. MOSIER

CONTRIBUTIONS TO ECONOMIC GEOLOGY

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This report describes silver minerals, especially a new variety of cryptomelane, and explains why unmined silver ores remain at the surface in this old mining district

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CONTRIBUTIONS TO ECONOMIC GEOLOGY

ARGENTIAN CRYPTOMELANE AND BROMARGYRITE IN VOLCANIC ROCKS NEAR SILVER CLIFF, COLORADO

By Fred A. Hildebrand and Elwin L. Mosier

ABSTRACT

This investigation of silver-bearing manganese veins and breccia fillings in rhyolitic rocks of Oligocene age in the Silver Cliff-Rosita mining district of south-central Colorado discloses that appreciable amounts of unmined silver ore remain at the surface. The remaining silver is mainly in argentian cryptomelane, a new variety identified during this study. Associated minerals are bromargyrite, goethite, dickite, fluorite, barite, and minor amounts of chalcophanite, todorokite, and birnessite. Although the study was directed mainly to the manganiferous silver ores, the base-metal fissure veins were also examined for the potential silver content of galena and sphalerite, and an explanation is offered for the long-misunderstood nature and processing of the manganiferous silver ores.

The amalgamation process of extraction recovered only the silver in bromargyrite, whereas mill tailings of manganese oxide containing 10-20 ounces of silver per ton were discarded. Argentian cryptomelane in outcrops and in waste materials that were cast aside as worthless commonly contains 500-3,000 parts per million silver and, in some instances, 5,000-10,000 parts per million silver.

Vein jarosites, heretofore unrecognized in the area, are associated with base-metal fissure veins and are accompanied by silver halides. The silver content of galena and sphalerite from the fissure veins was found to be 1,000-3,000 and 50-150 parts per million, respectively.

The Silver Cliff area appears to be unique in having appreciable argentian cryptomelane and bromargyrite, rather than chlorargyrite, distributed over a relatively large area. The presence of abundant bromargyrite indicates a large source of bromine from the volcanic parent rocks.

INTRODUCTION

Base-metal smelting ores were discovered in the Silver Cliff-Rosita mining district as early as 1863, and in 1878 manganiferous silver ore was discovered that assayed as much as 8,400 ounces of silver per ton. The manganiferous silver ores, however, like those in many other mining districts in the Western United States, were handicapped by metallurgical problems in processing. Poor recovery of silver from such ores, estimated to be only 65 percent, was a common problem, as illustrated by the presence of 10-20 ounces of silver per ton in the mill tailings of amalgamated manganiferous silver ores at Tombstone, Ariz. (Church, 1887, p. 605), and at Lake Valley, N. Mex. (Silliman, 1882, p. 435), as well as at Silver Cliff, Colo. (Irwin, 1881, p. 715). One of the principal metallurgical obstacles, apparently, has been the presence of a heretofore unrecognized variety of silver-bearing manganese oxide—argentian cryptomelane—that would not respond to amalgamation or cyanidation treatment. It has been positively identified at Silver Cliff (this paper) and at Tombstone,[1] but it has not yet been identified at Lake Valley. Thus, an understanding of the mineralogy of the ores will facilitate the solution of the metallurgical problem.

LOCATION AND EXTENT OF AREA

The area investigated is in the Silver Cliff-Rosita mining district, Custer County, Colo. (fig. 1), on the east side of the Wet Mountain Valley between the high Sangre de Cristo Range and the lower Wet Mountains. One main mining area is north of Silver Cliff, and the other is to the southeast around Rosita and Querida.

The manganiferous silver ores occur on the Silver Cliff Plateau from the vicinity of Silver Cliff eastward to Round Mountain (fig. 2). The Silver Cliff Plateau merges northward into the White Hills, where the ores occur mainly as base-metal fissure veins containing cerussite. This area was called the Carbonate Belt in some early reports. To the southeast the Rosita area contains many large and small base-metal fissure veins, a deep gold- and silver-bearing chimney opened by the Bassick mine at Querida, and a small area of manganiferous silver ore on Game Ridge (fig. 2).

Detailed sample-locality maps of the Silver Cliff and Rosita areas are shown in figures 3 and 5, respectively.

The senior author is responsible for the field and mineralogical studies and the junior author is responsible for most of the spectrographic data.

ACKNOWLEDGMENTS

We thank the many people of the Westcliffe-Silver Cliff area for providing information on mine locations and allowing access to properties and for other disclosures that could only be obtained from them.

We are grateful for the analytical assistance of several U.S. Geological Survey personnel, who are acknowledged individually at appropriate places in the report.

[1]During this study, an old analyzed sample of cryptomelane from Tombstone (USGS No. D-1237 cited by Richmond and Fleischer, 1942, p. 610), obtained from W. T. Schaller in approximately 1952, was reexamined and found to contain 500 parts per million silver. X-ray-diffraction patterns show only a single cryptomelane phase; thus, it is presumed to be argentian cryptomelane.

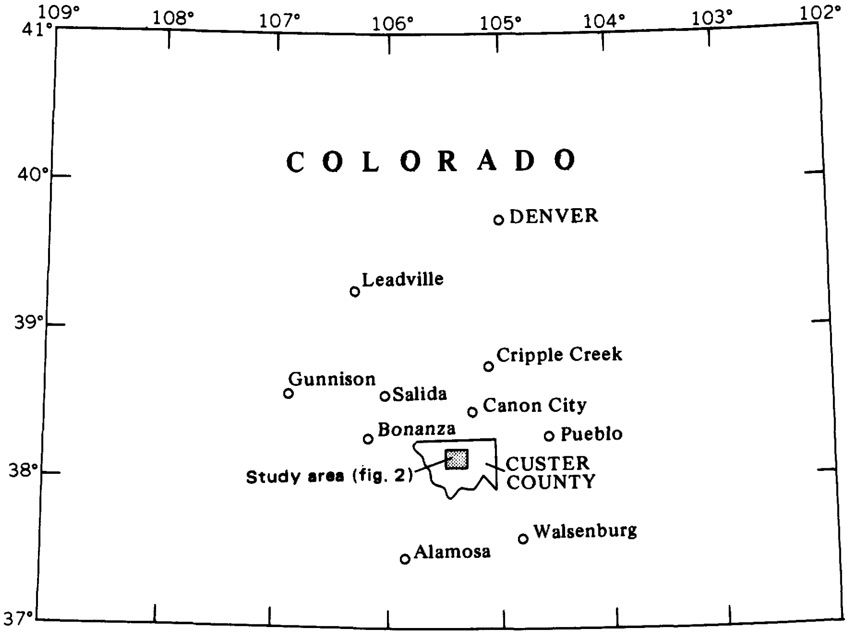


FIGURE 1.—Location of the study area in south-central Colorado.

MINING HISTORY

The first discoveries of ore were made near Rosita between the years 1863 and 1877. In 1878, rich "hornsilver" ore was discovered on a bluff at the north edge of what later became the city of Silver Cliff. The silver halide consisted of solid fist-size pieces of bright-green mineral that assayed 8,400 ounces of silver per ton (Wulsten, 1878) and was described as occurring in "pores" in the rock. The "pores" can still be seen on the uppermost remnants of the Silver Cliff bluff. They are partly lithophysae cavities in rhyolite and partly druses in manganese veins. The "hornsilver" discovery area near Silver Cliff was developed mainly by quarrying and became known as the Racine Boy quarry. A little later, the Silver Cliff quarry was developed adjacent to, and west of, the Racine Boy quarry. Surprisingly, the workings are virtually unchanged, as can be seen by comparing them with an 1888 photograph (Emmons, 1896, pl. 37). Consequently, materials that are comparable with the early mined ores can be obtained here to determine the mineralogy of the original ores that were processed by the then adjacent mills.

Extensive prospecting of the Silver Cliff Plateau led to many additional discoveries of silver halide there and on Round Mountain. Shortly thereafter, base-metal fissure veins similar to those in the Rosita Hills were discovered in the White Hills.

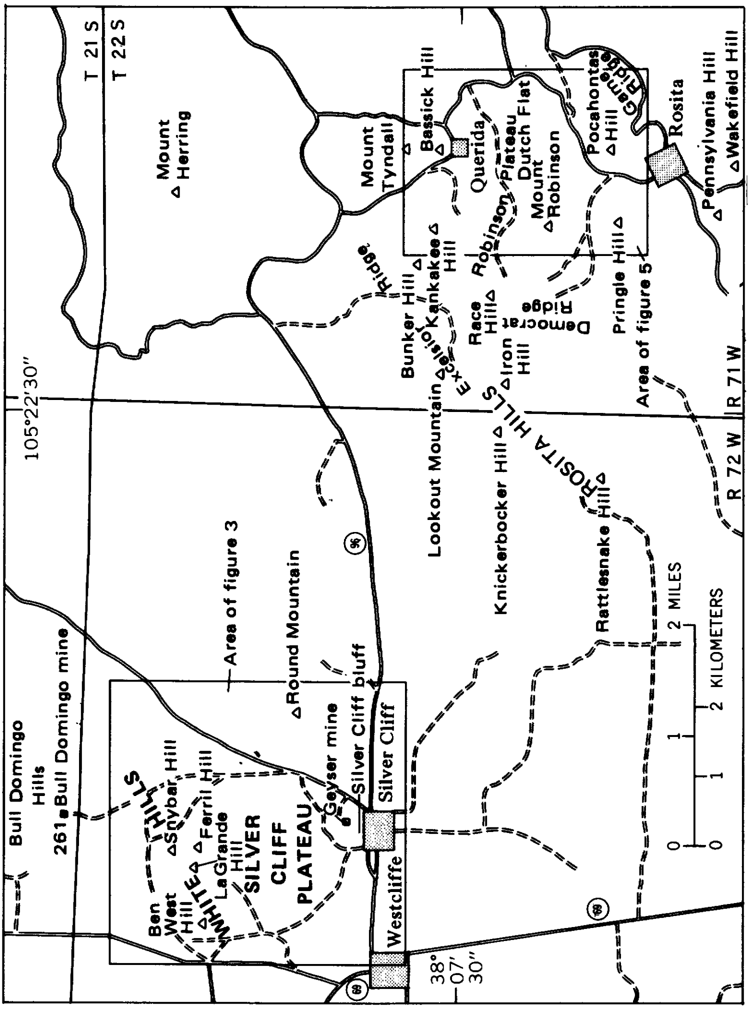


FIGURE 2.—Principal mining area of the Silver Cliff-Rosita mining district and areas of detailed sampling.

METHODS OF SAMPLING AND MINERALOGICAL STUDY

A method of sampling was chosen for collecting the material from veins, breccia, and dumps to give products resembling mill concentrates of manganiferous material containing as little rhyolitic rock and gangue minerals as possible. Materials from veins were collected over as long an interval as was practical to obtain a representative sample. The material from breccias consisted of a representative quantity of black matrix, free of rhyolite fragments. Dumps or other waste provided manganiferous material consisting of breccia matrix or vein material, or both.

Sampling of the Silver Cliff quarry area was directed toward the remaining outcrops of breccia and veins of manganiferous silver ore. Samples were collected from veins on the highest remaining parts of the Silver Cliff bluff and from breccia in the lowest accessible part of the Racine Boy quarry at the end of a tunnel that begins in the east wall of the Silver Cliff quarry, passes under, and ends beneath the floor of the Racine Boy quarry (fig. 4, locs. 63 and 64).

In the laboratory, the black manganese materials were handpicked and ultrasonically cleaned. From these preparations about 100-200 pieces of the purest appearing manganese material were then handpicked, crushed in a Plattner diamond steel mortar, and studied by X-ray-diffraction patterns and, occasionally, by X-ray fluorescence. Elemental determinations were made spectrographically. At first, fire-assay and atomic-absorption examinations were also made, but these analyses were discontinued after the results were found to agree well with the spectrographic method. To insure that all the silver was attributable to the manganese material and that there was no contribution of silver from silver halide, the samples were treated with ammonium hydroxide. Some samples containing unusually large amounts of silver, and therefore suspected of containing silver halide, were further examined for halogens by X-ray fluorescence; however, none was found.

From samples of base-metal fissure veins, tiny cleavage blocks of galena and transparent cleavage fragments of sphalerite, free of inclusions, were handpicked and ultrasonically cleaned. Their purity was ascertained by X-ray examination, and their silver content was determined spectrographically.

GEOLOGIC SETTING

The rocks of the Silver Cliff-Rosita mining district are of volcanic origin and, according to G. R. Scott and R. B. Taylor of the U.S. Geological Survey (oral commun., 1972), are of Oligocene age. The rocks were first mapped by Cross (1896) and recently by Siems (1967, 1968).

The rocks of the Silver Cliff Plateau (fig. 2) are mainly flow-banded platy rhyolite, spherulitic rhyolite, rhyolitic flow-breccia, and obsidian.

The White Hills consist mainly of rhyolitic tuffs, tuff breccias, several syenite (?) dikes, and small patches of quartz latite. The rocks and ore deposits of the Silver Cliff Plateau are different from those of the White Hills, partly because the plateau has been dropped considerably by faulting, and rocks higher in the geologic section are exposed, but also because both areas probably have different sources of mineralizing solution.

The rhyolitic rocks of the Silver Cliff Plateau and White Hills are bordered on the north and east sides by Precambrian granitic rocks. The enclosing rocks on the west and southwest sides are completely obscured by valley-fill deposits in the Wet Mountain Valley. The rhyolitic volcanic rocks extend southeast from Silver Cliff between bordering Precambrian granitic rocks to the Rosita Hills, as shown by Cross (1896, pl. 26). Thus, the volcanic rocks of the district have a northwest elongation which parallels the northwest trend of the largest fissure-vein system in the Rosita Hills, namely, the Humboldt-Pocohontas vein, bearing N. 50° W. (Siems, 1967, pl. 5). These lineaments indicate that the volcanic rocks probably gained access to the Precambrian granites along a broad northwest-trending zone of weakness.

Siems (1967, p. 161-165) contended that the volcanic rocks around Silver Cliff denote a part of a small calderalike structure with successive concentric-ring faults and that the rocks within the caldera have subsided more than 2,000 feet. Additional evidence observed currently, and in support of Siems' ring-fault concept, is the occurrence of two additional parallel faults south of an innermost ring fault in section 9 (Siems, 1967, pl. 3). This large fault was first noted by Cross (1896, p. 400). It bears about N. 70° W. and separates obsidian on its south side from rhyolitic tuffs and breccias.

Siems implied that the mineralized rocks in the White Hills may stem from a buried rhyolite dome located a short distance northeast of Ben West Hill. This concept is important to the current study because it affords a new source of mineralizing solution to explain why the ore minerals of the White Hills are different from those of the Silver Cliff Plateau.

ORE DEPOSITS

SILVER CLIFF PLATEAU AND ROUND MOUNTAIN

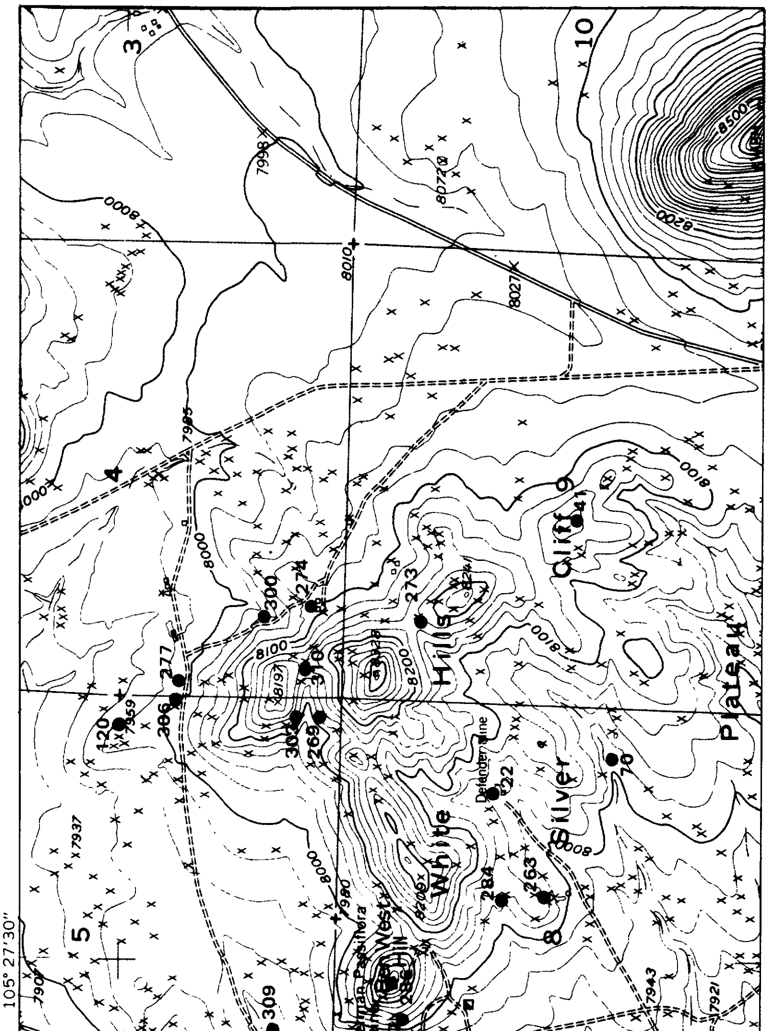
Many hundreds of workings, consisting of prospect pits, trenches, shafts, quarries, and tunnels, occur in the rhyolitic rocks on the Silver Cliff Plateau and eastward to Round Mountain (fig. 3). Most of the workings are shallow, and probably none exceeds a depth of 100 feet, with the exception of the 2,640-foot-deep exploratory Geyser shaft. Inspection of many workings disclosed that prospecting and mining were directed toward the exploitation of black manganiferous veins, stockworks of veins, and fillings around breccia fragments. In a few places the manganiferous material is concentrated around spherulites or it partially or wholly fills vugs and lithophysae cavities. There is no doubt that the sought mineral, which is clearly stated in many early reports to be "hornsilver" or "chlorsilver," was directly associated with the manganese concentrations of the types just described. One can readily see that the largest workings, which were also the best producing mines, were staked out where the manganese mineralization was most intense, because there, too, must have been the richest concentrations of silver halide. The most intense mineralization of this type is at the Racine Boy quarry and around the Kate mines (fig. 3).

The manganiferous silver ore occurs in flow-banded rhyolite and rhyolite breccia. Much of the Racine Boy quarry is in volcanic breccia, but the top of the Silver Cliff bluff is a flow-banded rhyolite containing, in places, large hollow lithophysae structures. The adjacent Silver Cliff quarry is predominantly in flow-banded and massive rhyolite in which manganese concentrations are less abundant.

The manganese concentrations in the breccias occur as matrix fillings around rhyolite fragments, but they also occur as small vuggy zones in both matrix and fragments. In the flow-banded ryholites, the manganese concentrations occur as veins and partial fracture fillings. The smaller veins have no regular structural pattern, but the larger ones trend either northwest or northeast and are generally vertical. The veins range in thickness from a hairline width to 5 inches, but for the most part they are ½–2 inches wide. Some veins are brecciated and contain fragments of rhyolite. In some fractures the manganese veining material does not completely fill the fracture but lines the walls and forms vuggy zones with botryoidal surfaces.

BROMARGYRITE

In the summer of 1965, Mrs. James Reilly, a lifetime resident of Silver Cliff, loaned specimens of silver ore to the senior author that were collected, to the best of her knowledge, from the Racine Boy quarry during the early mining days. Because of their rarity, they will be described in some detail. The specimens are rhyolite breccia and flow-banded rhyolite that contain abundant bright-green euhedral bromargyrite crystals. The crystals occur as single crystals and as clusters or chains of crystals of several isometric forms. They are most common in cavities in the rhyolite, but also occur as thin veinlets that cut goethite and the enclosing rhyolite, and, with cryptomelane, fill square tabular barite casts. Bromargyrite is intimately associated with bluish-black cryptomelane, brown and red goethite, brown and colorless fluorite, cloudy white barite, yellow dickite, and a very small amount of reddish-brown hematite. Goethite and hematite are partly pseudomorphous after a mineral that forms rhombohedrons and rosette clusters of rhombohedrons. The rhombohedral mineral presumably was ferroan rhodochrosite. It was identified by X-ray dif-


105° 27′30″
38° 10′
White
Hills
Silver
Cliff
Plateau
West
Defender mine
3
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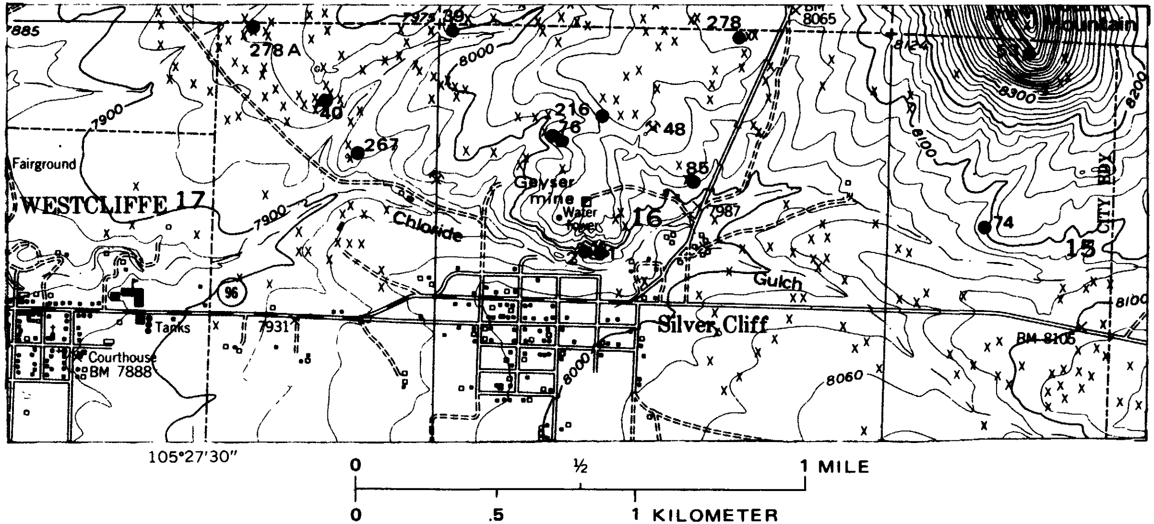

SAMPLE NUMBERS AND MINE OR QUARRY NAMES

1	Racine Boy	74	Horn Silver	274	Lady Franklin	303	Valley
2	Silver Cliff	76	King of the Valley	277	Reveille	305	Songbird
22	Defender	85	Hecla	278	Chalcedon	306	Keystone
39	Buffalo	120	Immortal	278A	Kate (north)	307	Thames River
40	Kate (Silver Bar)	216	Obsidian (Calumet-Victor)	284	Moultrie	308	Herman
41	Vanderbilt	263	King of the Carbonates	286	Ben West	309	Gray Eagle
48	Buffalo Hunter	267	Ruby Cliff	299	Passiflora (north)	310	Black Friday
53	Plata Verde	269	Maxine Elliot			311	Passiflora (south)
70	Jay Gould	273	Orange	300	Sunrise		

FIGURE 3.—Sample localities in the Silver Cliff area.

fraction from pieces of cores in which fresh pale-pink rosettelike clusters of rhombohedrons occur in vuggy areas. X-ray studies showed that these ferroan rhodochrosites have a ratio of Mn : Fe≈60 : 40. The presence of ferroan rhodochrosite is noteworthy because in an acid environment it could serve as a source for manganese and iron. The core samples from localities 278 (at 89-ft depth) and 278A (at 586-ft depth, fig. 3) were provided by Joe Chelini of Callaghan Mining Co. and by Dolf Fieldman of Congdon and Carey, Ltd., respectively.

Some of the silver-bearing manganiferous materials collected from the quarries for this study also contain rare tiny pieces of bright-green bromargyrite enclosed by cryptomelane or goethite. Some of the bromargyrite is coated with a thin layer of elemental silver. The coated mineral has a purplish-gray waxy appearance and an adamantine luster much like chlorargyrite (silver chloride), but beneath the coating, it is bright green. X-ray-diffraction and fluorescence examinations disclosed that it is single-phase bromargyrite in which neither chlorine nor iodine can be detected at the lower 0.1 percent limit of sensitivity.

Bromargyrite was identified in specimens from outcropping breccia in the Racine Boy quarry (fig. 4, loc. 16), an outcropping manganese vein northeast of the quarry (fig. 4, loc. 44), an outcropping manganese vein on top of the Silver Cliff bluff (fig. 4, loc. 13), and a large dump at the south edge of the Silver Cliff quarry (fig. 4, loc. 45). A 10-pound sample of rhyolitic dump rock from locality 45 was found by fire assay to contain 8½ ounces silver per ton. A portion of a sample collected from this locality and concentrated by wet sluicing in 1962 was given to us by Bill Klein of Silver Cliff. It contained bromargyrite and argentian cryptomelane and was found by fire assay to contain 390 ounces of silver per ton.

CRYPTOMELANE

Cryptomelane, essentially potassium manganese oxide, is the most abundant mineral of the manganiferous veins and breccia fillings. It is hard and brittle and adheres tightly to the rhyolitic wallrock of veins and to rhyolitic breccia fragments. The cryptomelanes have a dull submetallic to shiny metallic luster, a bluish-black to grayish-black color, and a rough, uneven to smooth conchoidal fracture. X-ray and spectrographic examinations of many cryptomelanes with these variable physical properties disclosed, surprisingly, that they are all of a single phase and vary only slightly in degree of crystallinity and elemental composition. Approximately 50 cryptomelanes from the Silver Cliff quarries have identical X-ray interplaner spacings. A silver content of 10,000 p/m (parts per million) produced no observable structural change.

Cryptomelanes from outcrops near and in the Racine Boy quarry and on the Silver Cliff bluff contain from 500 to as much as 10,000 p/m silver; the average silver content of 45 cryptomelanes is 2,500 p/m.

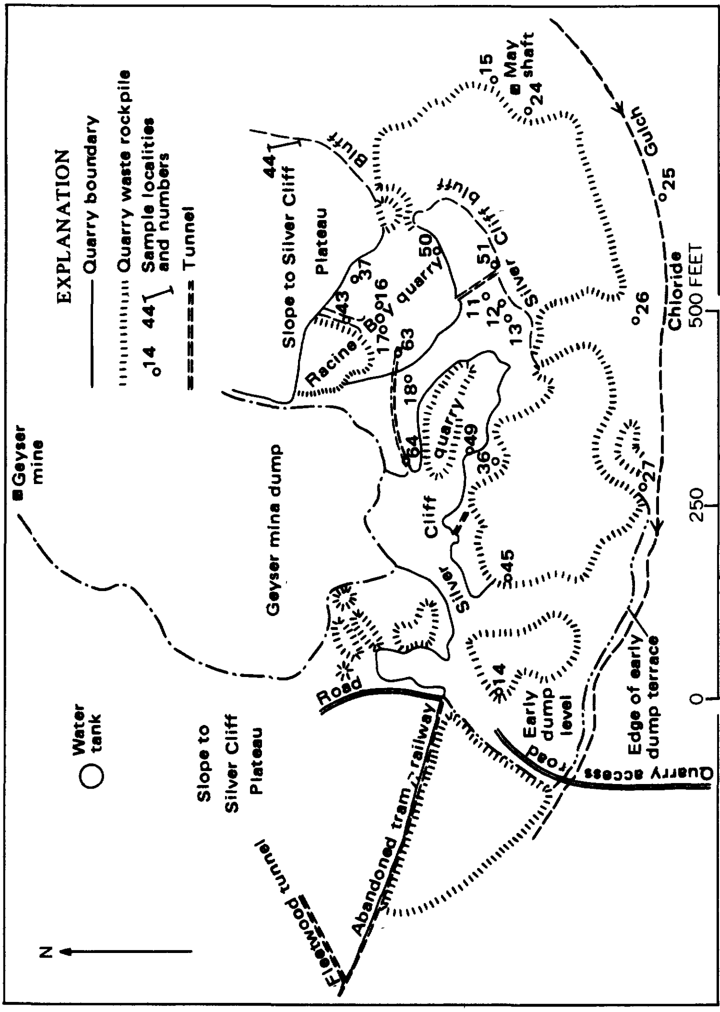

FIGURE 4.—Pace-and-compass map of the Racine Boy-Silver Cliff quarry area, showing sample localities.

Other samples from the northwest corner of the Silver Cliff quarry, however, contain only 100-200 p/m silver.

The localities and source data of cryptomelanes containing more than 4,000 p/m silver are presented in table 1.

The maximum amount of silver in cryptomelane from the Silver Cliff quarries, as shown in table 1, is 1 percent. Cryptomelane containing 1 percent silver was also found at other mines on the Silver Cliff Plateau and at Round Mountain, cited later in this report. The silver-bearing cryptomelane of this area is argentian cryptomelane, reported here as a new variety.

The compositional and structural properties of cryptomelane which has the αMnO_2 structure were studied in considerable detail by Gruner (1943) and Byström and Byström (1950). Barium, lead, and silver cations, which have large ionic radii similar to that of potassium, can proxy for potassium as in the high-barium mineral hollandite and the high-lead mineral coronadite. No correspondingly high-silver cryptomelane has, to our knowledge, been reported to occur. The presence of such large cations, especially potassium, apparently is necessary for the formation of cryptomelane and to prevent the structure from

TABLE 1.—*Occurrences of cryptomelane containing 4,000 p/m or more silver in the Silver Cliff quarry area*

Locality (fig. 4)	Nature of occurrence	Number of pieces	Silver content (p/m)
11	½-inch-wide veinlike concentration from topmost part of Silver Cliff bluff.	5	[1]4,000
16	Quarried block (B-3) from waste pile on floor of Racine Boy quarry.	20	4,000
15	Dump near northeast corner of May shaft.	3	[1]4,000
51	1-inch-wide veinlike concentration from upper south face of Silver Cliff bluff.	50	4,000
63	Matrix of rhyolitic breccia from 30-ft-long interval at end of tunnel beneath floor of Racine Boy quarry.	200	5,000
49	From 30-ft-long interval of 1½-inch-wide vertical vein trending N. 45° W. along quarry bench.	40	5,000
16	Quarried block (B-1) from waste pile on floor of Racine Boy quarry.	25	7,000
44	From 50-ft-long interval of trenched 1- to 2-inch-wide vertical vein trending N. 15° W. in outcrop.	20	7,000
16	Quarried block (B-2) from waste pile on floor of Racine Boy quarry.	20	10,000

[1]Content of each piece.

collapsing. The composition of the cryptomelane that forms depends upon what elements are available in the solutions at the time of formation, and, mainly for this reason, the K^{+1}, Ag^{+1}, Pb^{+2}, and Ba^{+2} content can vary, as shown by compositional data from the Silver Cliff area cited later in this report.

Gruner (1943, p. 503) stated that numerous cation substitutions are possible including some between manganese ions of different sizes and ionic charge. The states of oxidation of manganese partly determine how much K^{+1}, Ba^{+2}, Pb^{+2}, and Ag^{+1} can enter the structure at the time the minerals form. Supposedly, more silver, which has a one-positive charge, can enter the structure than barium and lead, each of which has a two-positive charge. The substitutions cause some lattice distortion and instability, especially in the cryptomelanes with the larger cations.

Gruner (1943, p. 500, 504) synthesized a cryptomelane containing 13.7 percent silver from an artificial reagent—manganese oxide that was structurally cryptomelane and initially contained 3.1 percent potassium oxide but no silver. To explain the introduction of the large amount of silver into the structure, Gruner presumed that only some of the potassium ions were replaced by silver and that some silver entered "open positions" or "holes" in the structure, but some may have just been adsorbed. He further postulated that some monovalent silver may be reduced to metallic silver by Mn^{+2} ions. As an atom, it could fit into the "open positions" or "holes" which are sufficiently large to store water, as in the zeolite minerals.

If silver, lead, and barium partly proxy for potassium, cryptomelanes containing larger amounts of these elements should contain lesser amounts of potassium. To ascertain these relationships the potassium and silver contents of five cryptomelanes from the Racine Boy and Silver Cliff quarries were determined and are shown in table 2. This table shows that cryptomelanes of high silver content contain less potassium than cryptomelanes of low silver content and that as the silver increases, the potassium decreases. Also noteworthy in table 2 is the observation that the cryptomelane with the least potassium has the greatest total cation content, consisting of the cations silver, lead, barium, and strontium totaling about 73,000 p/m, whereas the cryptomelane with the most potassium has the least total cation content of about 2,300 p/m.

Several cryptomelanes with higher than average barium and lead were noted from the Racine Boy quarry. Most notable is one containing about 7 percent barium and 0.7 percent silver and another containing about 7 percent lead and 1 percent silver. These cryptomelanes do not contain sufficient barium or lead for them to be called hollandite or coronadite, but their X-ray-diffraction patterns are somewhat different from those of normal cryptomelane in that some lines show shifting and intensity differences.

TABLE 2.—*Major cation constituents of five cryptomelanes from the Racine Boy and Silver Cliff quarries*

[Potassium determinations were made by Kam Wo Leong, all other determinations were made by Elwin L. Mosier, both with the U.S. Geological Survey]

Sample	Loc. (fig. 4)	K (per cent)	Ag (p/m)	Ba (p/m)	Sr (p/m)	Zn (p/m)	Pb (p/m)	Fe (per cent)	Approximate total major cations[1] (p/m)	Approximate total major cations[1] (percent)	X-ray phases shown
Ag 15-B	15	3.6	100	1,000	1,000	5,000	200	2.0	7,300	0.7	Cryptomelane, trace of goethite and quartz.
Ag 14-C	14	3.3	1,000	1,000	2,000	7,000	2,000	1.5	13,000	1.3	Cryptomelane, trace of quartz.
Ag 16-A-1	16	2.8	1,000	>30,000	1,500	10,000	200	.7	>42,700	4.3	Cryptomelane, trace of quartz.
Ag 11-D-5	11	2.0	4,000	20,000	3,000	30,000	>20,000	1.0	>77,000	7.7	Cryptomelane, trace of quartz.
Ag 16-B-1	16	1.3	7,000	≈60,000	1,000	15,000	5,000	10.0	≈88,000	8.5	Cryptomelane, moderate amount of goethite.

[1]Excluding K and also Fe, most of which is assumed to be in goethite.

TODOROKITE AND CHALCOPHANITE

Todorokite (Mn, Ba, Ca, Mg)$Mn_3O_7 \cdot H_2O$ was tentatively identified in one specimen of vein cryptomelane from the Silver Cliff quarry. Chalcophanite (Zn, Mn, Fe)$Mn_2O_5 \cdot 2H_2O$ associated with zinc-bearing cryptomelane was tentatively identified in a specimen of breccia filling from the Racine Boy quarry. Apparently, todorokite and chalcophanite are of sparse occurrence in the quarry area, and they could be tentatively identified in only the two specimens cited above.

GOETHITE, DICKITE, FLUORITE, AND BARITE

Goethite, dickite, fluorite, and barite are coevally associated with cryptomelane and bromargyrite, and all these minerals are believed to be of volcanic hydrothermal origin. They occur in vugs of breccia fillings and in elongated vugs that parallel the wallrock contact of manganese veins.

Goethite varies widely in color from black, brown, tan, and red to orange-yellow and yellow. Goethite accompanying bromargyrite is commonly bright shiny red and shows internal reflections. Pseudomorphs of goethite after a rhombohedral mineral are uncommon, as in the Reilly specimens described earlier in this report. Minor amounts of goethite as thin iridescent films are probably the result of recent weathering.

Dickite is abundant and is fine grained, sugary, and tan to orange yellow and yellow and cannot be distinguished from geothite in the field. Presumably, because of the identical appearance of the two minerals, much dickite in this area has formerly been misinterpreted to be goethite.

Fluorite occurs as clear, brown, green, and, more rarely, purple clusters of cubes embedded in cryptomelane, goethite, or dickite. In some places it has been leached, leaving only casts, some of which still contain remnants of unleached fluorite. Barite occurs most commonly as aggregates of tabular crystals, some trending toward prismatic habit with a length of as much as 1½ inches. Some of it has been leached leaving tabular-shaped casts, and, in some casts, small remnants of solution-pocked barite still remain.

Other ore deposits of the Silver Cliff Plateau and Round Mountain, as seen in the mines and exploratory workings, are so similar to those of the Silver Cliff quarry area that their descriptive mineralogy will not be repeated; instead, it is tabulated (table 3). The studied cryptomelanes contain 100 p/m or more of copper, antimony, vanadium, cadmium, and bismuth, and lesser amounts of minor elements, as shown in table 4. Their average elemental composition is in the range shown for analyzed cryptomelanes, as cited by Richmond and Fleischer (1942, p. 610).

WHITE HILLS

The base-metal fissure veins of the White Hills supplied refractory silver ores that contributed to the early silver production of the district. The ore minerals containing silver, lead, zinc, and smaller amounts of copper occur in stringer zones in veins that range in width from less than 1 to 10 feet.

Mineralogic studies were made of fresh specimens from two recently operated mines, the Maxine Elliot and the Reveille (fig. 3). Specimens from the 100-foot level of the Maxine Elliot, kindly supplied by the owner, James Turner of Silver Cliff, disclose that the mineral assemblage is mainly pyrite, galena, 2M-type sericite mica, barite, anglesite, cerussite, sphalerite, goethite, and quartz. The silver contents of bright silver-gray and dull black sooty galena are reported in table 5.

Specimens from the Reveile mine, kindly supplied by the owner, Pete Cowan of Westcliffe, came from the 100-foot level of a new drift along the original Reveille vein. The vein had not been previously mined westward beyond an intersecting syenite dike. By trenching the unexplored area west of the syenite dike, Cowan exposed the vein just a few feet below the surface, where it is 4-6 feet wide and contains stringers of solid galena 4-6 inches wide. Surprisingly, this area, with ore just beneath the surface, apparently had not been explored even during extensive prospecting of the early mining days. The mineral assemblage is like that of the Maxine Elliot vein cited previously. Black galena, thought by the miners to possibly be acanthite, was found to have a normal unit-cell size. The silver contents of black and silver-gray galena from the Reveille mine are shown in table 5.

TABLE 3.—*Minerals of Silver Cliff Plateau and Round Mountain mines*

Mine	Locality (fig. 3)	Mineral	Remarks
Ruby Cliff	267	Argentian cryptomelane.	Dull black cryptomelane in veins and vuggy zones in fine-grained platy rhyolite.
		Chalcophanite	Brilliant black radiating-fibrous fanlike masses and spherical forms with structureless gray centers. Also as cross-fiber bands and pimply botryoidal crusts. Occurs sparsely with todorokite and cryptomelane. Non silver bearing.
		Todorokite	Dull or shiny radiating bundles and plumose masses with confused fibrous leafy structure and silky sheen. Non silver bearing.
		Goethite	With cryptomelane in pseudomorphs after rhombic ferroan rhodochrosite (?). Also with cryptomelane and in pseudomorphs after cubic fluorite in which remnants of fluorite still remain.
		Fluorite	Colorless, brown, and purple; cubic forms.
		Dickite	Sugary orange-yellow coatings on fluorite. Also as veins cutting through fluorite cubes.
Kate (Silver Bar).	40	Bromargyrite	Found in three specimens as bright-green pellets, 1-2 mm in diameter, and as purple-coated euhedral isometric crystals or clusters of rounded crystals associated with reddish-brown goethite and tan dickite in cryptomelane veins in flow-banded and platy rhyolite. Also found as a bright-green pellet, 1 mm in diameter, enclosed by a thin radial-fibrous layer of brilliant reddish-black chalcophanite, both enclosed in a ½-inch-wide vein of black cryptomelane containing 1 percent silver.
		Argentian cryptomelane.	Hard brittle black ½-inch-wide vein of cryptomelane containing 1 percent silver. X-ray fluorescence shows there is no contribution of silver from bromargyrite. 13 other specimens show silver values ranging from 500 p/m for pieces containing goethite as a diluent to 5,000 p/m for pieces of pure cryptomelane. The arithmetic mean of 14 determinations is about 3,000 p/m silver.
		Fluorite	Clear, brown, and purple cubic forms.
		Dickite	Sugary orange-yellow coatings.
		Goethite	Brown, red, and black masses closely associated with cryptomelane.
		Chalcophanite	Occurs as a coating around kernel of olive-green bromargyrite, the whole enclosed by argentian cryptomelane in the ½-inch-wide vein specimen cited above. Has brilliant luster, radial-fibrous habit, and deep red internal reflections. Closely resembles goethite.
Obsidian quarry (Calumet-Victor).	216	Birnessite (ΔMnO_2)	Small black soft fragile nodular masses of irregular shape intimately mixed with cryptomelane in montmorillonitic clay in the outer margin of a large spherulite, 7 ft in diameter, in obsidian.
		Cryptomelane	Poorly crystalline and intimately associated with birnessite described above. No silver could be detected in a mixture of the cryptomelane and birnessite.
		Montmorillonite	Formed by devitrification of glassy obsidian.
Hecla (trench)	85	Birnessite (?)	Closely associated with argentian cryptomelane and goethite. Manganese minerals occur as a matrix filling around silica fragments in spherulitic rhyolite.

Table 3.—*Minerals of Silver Cliff Plateau and Round Mountain mines*—Continued

Mine	Locality (fig. 3)	Mineral	Remarks
		Argentian cryptomelane.	Hard, brittle, smooth, bluish black. Contains 1,500 p/m silver.
		Goethite	Orange yellow. Closely resembles dickite. Vug fillings.
		Botryoidal silica.	Creamy brown. Lines walls of vugs.
Jay Gould	70	Galena	See table 5.
		Argentian cryptomelane.	Contains 500 p/m silver.
		Lead, manganese oxide.	Unidentified. Not coronadite or quenselite.
Buffalo (trenches).	39	Bromargyrite	Tiny irregularly shaped bright-green pieces found in ultrasonically cleaned samples of black botryoidal cryptomelane from veins, about 8 inches wide, in platy rhyolite.
		Argentian cryptomelane.	2- to 4-inch-wide veins with large botryoidal surfaces in some places. Some botryoids are nearly 3 inches in diameter. 13 specimens contain 20-700 p/m silver and average 200 p/m silver. Five specimens contain 1,000-2,000 p/m silver.
		Barite	Local concentrations in cryptomelane.
King of the Valley	76	Argentian cryptomelane.	Smooth, bluish black. In thin veinlets and as thin coatings on spherulites in rhyolite. Aggregate of 20 pieces contains 300 p/m silver.
		Goethite	Smooth, shiny, black.
		Barite	Colorless plates.
		Dickite	Sugary, orange yellow.
Vanderbilt	41	Bromargyrite	Small olive-green-, bright-green-, or purplish-coated masses associated with dark-red goethite in 12 specimens from bluish-black cryptomelane veins in rhyolitic tuff.
		Argentian cryptomelane.	Thin veins in fine-grained rhyolitic tuff. Six samples contain 200-700 p/m silver. Five samples contain 2,000-4,000 p/m silver. There was no contribution of silver from bromargyrite. One specimen containing 4,000 p/m silver and much greater than 2 percent lead is comparable to a high-lead cryptomelane from the Racine Boy quarry cited elsewhere in this report. Specimen also contains an unidentified lead manganese oxide structurally related to the unidentified lead manganese oxide from the Jay Gould mine cited above. Emmons (1896, p. 452) cited a ⅛-inch-wide manganese oxide vein containing 60 ounces (2,000 p/m) silver per ton.
		Barite	Abundant in all Vanderbilt ore.
		Dickite or goethite.	Orange yellow. Identity not established.
Buffalo Hunter	48	Bromargyrite	Tiny irregularly shaped bright-green pieces in two ultrasonically cleaned samples of bluish-black cryptomelane from small veins in flow-banded rhyolite.
		Argentian cryptomelane.	Samples from 20-ft-deep open trench trending N. 22° E. for about 600 ft. Widens into open-pit area at northeast end and presumably was trenched along a vein system. Mostly flow-banded rhyolite, but south end of trench is in spherulitic rhyolite, and the argentian cryptomelane from there contains 30 p/m silver. Eight specimens of smooth black botryoidal cryptomelane from flow-banded rhyolite north of the spherulite zone contain 1,000-10,000 p/m silver and have an

TABLE 3.—*Minerals of Silver Cliff Plateau and Round Mountain mines*—Continued

Mine	Locality (fig. 3)	Mineral	Remarks
			average silver content of 3,000 p/m. A loose slab of cryptomelane vein material measuring 4x12x1 inches from floor of trench near north end of zone contains 2,000 p/m silver.
			Clevenger and Caron (1925, p. 9, 22, 80) concluded from gas-reduction experiments on manganiferous silver ores, including Buffalo Hunter ore, that an unidentified refractory silver manganite compound is uniformly disseminated throughout a higher oxide of manganese, which they thought was psilomelane in the Buffalo Hunter ore. The current study shows, however, that only one silver-bearing manganese mineral, namely argentian cryptomelane, occurs in the ore.
Plata Verde	53	Argentian cryptomelane.	Stockwork of manganese veins trending northeast and northwest. Samples and average silver content as follows: 17 pieces of smooth black cryptomelane from a dump, 1,000 p/m (a single piece, 2,000 p/m); 9 pieces of smooth black rough-textured cryptomelane from waste rock in a small quarry, 300 p/m; 200 pieces of smooth black cryptomelane from a small vein bearing N. 80° E., 300 p/m; 50 pieces of hard brittle bluish-black cryptomelane from a small vein bearing N. 20° W., 600 p/m; 25 pieces of hard brittle bluish-black cryptomelane from trenched veins, 200 p/m; 6 pieces of smooth black cryptomelane from around the collar of a shaft in trench, 400 p/m.
	Exact location unknown.	"Psilomelane" cryptomelane.	Emmons (1896, p. 451) cited a sample of manganese oxide from south of Round Mountain. The 3.4 percent K_2O reported indicates to us that the mineral is cryptomelane and not psilomelane, in agreement with Hewett and Fleischer (1960, p. 21).
		Barite	White.
		Goethite	Black and brown.
Horn Silver	74	Bromargyrite	Tiny irregularly shaped bright-green masses from two specimens of bluish-black cryptomelane containing 1 percent silver.
		Argentian cryptomelane.	Small veins in rhyolite and bedded tuff. Samples and average silver content as follows: 2 pieces of black cryptomelane from a large dump, 50 p/m; 5 pieces of black and bluish-black cryptomelane, 100 p/m; 4 pieces of black cryptomelane, 450 p/m; 5 pieces of bluish-black cryptomelane, 1,800 p/m; 1 piece of bluish-black cryptomelane, 7,000 p/m, and another shiny black piece, 1,000 p/m; 1 loose piece of black cryptomelane from the shaft collar, 2,000 p/m. This cryptomelane is from a mirrorlike surface of a slickensided fault plane. The cryptomelane is polished by the movement. It shows plucking and is impure with grains of fault gouge in places. There was no contribution of silver from bromargyrite. The cryptomelane is obviously of prefault age.
		Barite	Large tabular crystals.
		Goethite	Brown and black. Probably contaminates and dilutes some cryptomelane samples and causes an apparent reduction in silver value.

TABLE 4.—*Elemental composition of cryptomelanes from 66 localities in the Silver Cliff area*

Element[1]	Number of samples	Average content	Element[1]	Number of samples	Average content
		percent			*p/m*
Pb	193	1.5	Ce	27	15
Zn	195	1.0	Nb	41	15
Ba	196	0.7	Ti[3]	27	15
Sr	195	0.15	W	194	<50
Ag	200	0.15	Bi (low values only)[2]	169	<20
		p/m			
Bi (high values only)[2]	27	500	Sn	194	<10
Cu	170	200	Se[4]	27	<10
Sb	21	200	Ge	127	<10
V	194	150	Yb	27	10
Cd	194	100	Sc	78	7
Y	195	70	Be	168	5
Ti	97	70	In[3]	27	2
Mo	194	70	Hg[5]	27	<0.2
La	41	30	Te[6]	27	<0.1
Nd	27	30	Au[7]	23	<0.1
Nd	27	30	Ta[3]	27	([8])
Zr	79	20	Pt[3]	27	([9])
Co	74	20			
Ni	191	20			

[1]All determinations by semiquantitative spectrographic analysis by E.L. Mosier, except as noted.
[2]The two high- and low-value groups for Bi were not averaged together, because of their distinctly different values. The high-value group came from near the boundary between the Silver Cliff Plateau and the White Hills, close to the base-metal fissure veins. The low-value group came from the Silver Cliff Plateau.
[3]Semiquantitative spectrographic analyses by Nancy M. Conklin.
[4]X-ray-fluorescence analyses by J. S. Wahlberg.
[5]Atomic-absorption analyses by W. W. Janes.
[6]Catalytic Te analyses by R. L. Turner.
[7]Atomic-absorption analyses by E. P. Welsch, J. R. Watterson, and A. E. Hubert.
[8]Not detected at 200 p/m.
[9]Not detected at 30 p/m.

Mineralogically, the fissure veins of other mines in the White Hills are very similar to the Maxine Elliot and Reveille veins. Galena from dumps of other mines contains comparable amounts of silver (table 5).

During the investigation of fissure veins, many occurrences of associated jarosite, a heretofore unrecognized mineral in the district, were found. It was positively identified from 12 mines (fig. 3): Ben West, Thames River, Moultrie, Passiflora (south), Herman, Songbird, Gray Eagle, Valley, Keystone, Sunrise, Black Friday, and Orange. Brown jarosite is still unrecognized by present miners, and for many years it has been referred to by them as "jasper" and "brown carbonate." At some mines it can be plainly seen in the upper part of the shaft as stringers in the fissure veins. A detailed study of a 2-foot-wide jarosite vein on Ben West Hill disclosed that jarosites with a wide range of composition and several stages of multiple injection occur in

TABLE 5.—*Minor elements[1] in galena and sphalerite from the Silver Cliff-Rosita mining district*

[Data shown in italic refer to sphalerite samples; all other data refer to galena samples. N, not detected at limit of detection N(Bi) = 10 p/m, N(Sb) = 150 p/m, N(Zn) = 200 p/m]

Mine	Sample[2] (Ag-)	Sample: Number of pieces	Sample: Source and remarks	Minor element content (p/m): Ag	Bi	Sb	Zn	Pb
Silver Cliff area mines (fig. 3)								
Defender	22-A	150	Ore shoot	1,500	N	1,500	3,000	.....
	-B	*50*	*...do*	*150*	.....	.....	.....	*300*
Jay Gould	70-A-1	10	Dump	1,000	20	1,000	<200	.....
King of the Carbonates (south shaft).	263-A-1	50	...do	1,500	15	1,500	N	.....
	B-2	*100+*	*...do*	*15*	.....	.....	.....	*100*
King of the Carbonates (north shaft).	263-B-1	110	...do	1,500	15	1,500	3,000	.....
Passiflora (north)	299-A	60	Loading dock; some trapped pyrite and sphalerite.	700	30	700	15,000	.....
Herman	308-A	100	Dump	700	20	300	N	.....
	-B	*30*	*...do*	*70*	.....	.....	.....	*150*
Songbird	305-A	100	...do	300	30	N	7,000	.....
	-B	*50*	*...do*	*100*	.....	.....	.....	*300*
Gray Eagle	309-A	100	...do	1,500	30	1,000	N	.....
	-B	*50*	*...do*	*150*	.....	.....	.....	*700*
Maxine Elliot	269	100	Dump; fresh, silvery	400	.....	.....	.....	.....
		.....	Dump; black sooty powder	550	.....	.....	.....	.....
	67-A	1	100-ft level; silver gray	700	N	700	30,000	.....
Reveille	277-1	100	Drift at 100-ft level; bluish black.	2,000	N	1,500	N	.....
	-2	100	Drift at 100-ft level; bright silver gray.	2,000	N	1,500	N	.....
Immortal smelter site	120	1	Dump	1,000	N	1,000	3,000	.....
Bull Domingo	261-A	20	...do	300	N	N	15,000	.....
Sunrise	300-A	15	...do	3,000	300	1,500	N	.....
Lady Franklin	274-A-1	8	Loading dock	700	N	500	700	.....
	-A-2	1	...do	200	N	N	N	.....
	-A-3	1	...do	1,000	N	700	N	.....
Rosita-Querida area mines (fig. 5)								
Senator (Maverick)	128	4	Dump; bluish black	1,500	300	N	N	.....
Maine No. 2	250	1	Shaft collar	1,500	N	700	3,000	.....
Vulcan	218	1	Dump	3,000	N	7,000	15,000	.....
Ben Franklin	249-A	18	Shaft collar; some trapped pyrite and sphalerite.	5,000	<15	10,000	20,000	.....
	-C-2	*50*	*Dump*	*70*	.....	.....	.....	*50*
	-B	210	Shaft collar	5,000	N	7,000	7,000	.....
	-C-1	1	...do	3,000	N	3,000	3,000	.....
Bunker Hill (northeast slope).	215	25	Dump; slightly impure with pyrite and sphalerite.	1,500	300	1,000	10,000	.....

[1] Semiquantitative spectrographic analyses by Nancy M. Conklin of the U.S. Geological Survey.

[2] Sample localities are shown in figures 3 and 5, except for the Bull Domingo sample 261, which is 3,800 ft N. 34° E. of locality 120 (fig. 3) and is shown in figure 2.

the same vein. Most of this vein was mined for its silver content during World War I. Silver halides were tentatively identified in remnants of this vein, collected from near the borders. They consist of iodian bromargyrite iodyrite and two others containing large amounts of iodine and smaller amounts of bromine and chlorine. The discovery of iodine-bearing silver halides supports oral statements by local miners concerning soft grayish-yellow clayey masses that occurred in mines from the Thames River southeastward toward the Defender mine. According to the miners, the clayey masses were yellow when freshly mined, but upon exposure to the sunlight for some time, they turned pale blue. The miners attribute the color change to an iodine content.

ROSITA HILLS

FISSURE VEINS

The volcanic rocks in the Rosita Hills are more andesitic and appear to consist of fewer rhyolitic flows and breccias than the volcanic rocks of the Silver Cliff area. Hydrothermal alteration is extensive over several broad areas, and there is only a small amount of manganese mineralization. The ore deposits are mainly base-metal fissure veins, as in the White Hills north of Silver Cliff, but here the veins are larger, and the mines are deeper. The large Humboldt-Pocahontas vein, for example, was mined for a distance of about 4,000 feet along its strike, and the Humboldt mine was 800 feet deep. Because the Rosita mines are now abandoned, specimens of galena and sphalerite for silver determinations (table 5) were collected mainly from dumps.

MANGANIFEROUS SILVER ORE AT GAME RIDGE

On the basis of early mining reports which state that "free milling," "hornsilver"-type ore occurs at Game Ridge, northeast of Rosita (fig. 5) (Irwin, 1881, p. 716; Engineering and Mining Journal, 1880), specimens from the Tecumseh mine were collected and studied. Cryptomelane and bromargyrite were identified from veins in what appears to be altered trachyandesitic rock. Dull black cryptomelane occurs as small veins and as weak botryoidal coatings on the walls of small vugs. X-ray-diffraction patterns show that the cryptomelane has good crystallinity, and spectrographic analyses disclose that it contains 4,000 p/m silver and is, therefore, argentian cryptomelane. The bromargyrite is olive green and occurs in the argentian cryptomelane, as well as in reddish-tan goethite and between tabular plates of white barite. The bromargyrite has a slightly smaller cell than normal, presumably because of small amounts of iodine and chlorine which were detected by a closed tube test. Goethite also occurs as reddish-brown pseudomorphs after a rhombohedral mineral similar to that previously described from the Silver Cliff Plateau.

CONCLUSIONS

The long-misunderstood nature of manganiferous silver ores and the difficulties experienced in their processing, at least at Silver Cliff, can now be explained on the basis of their mineralogy.

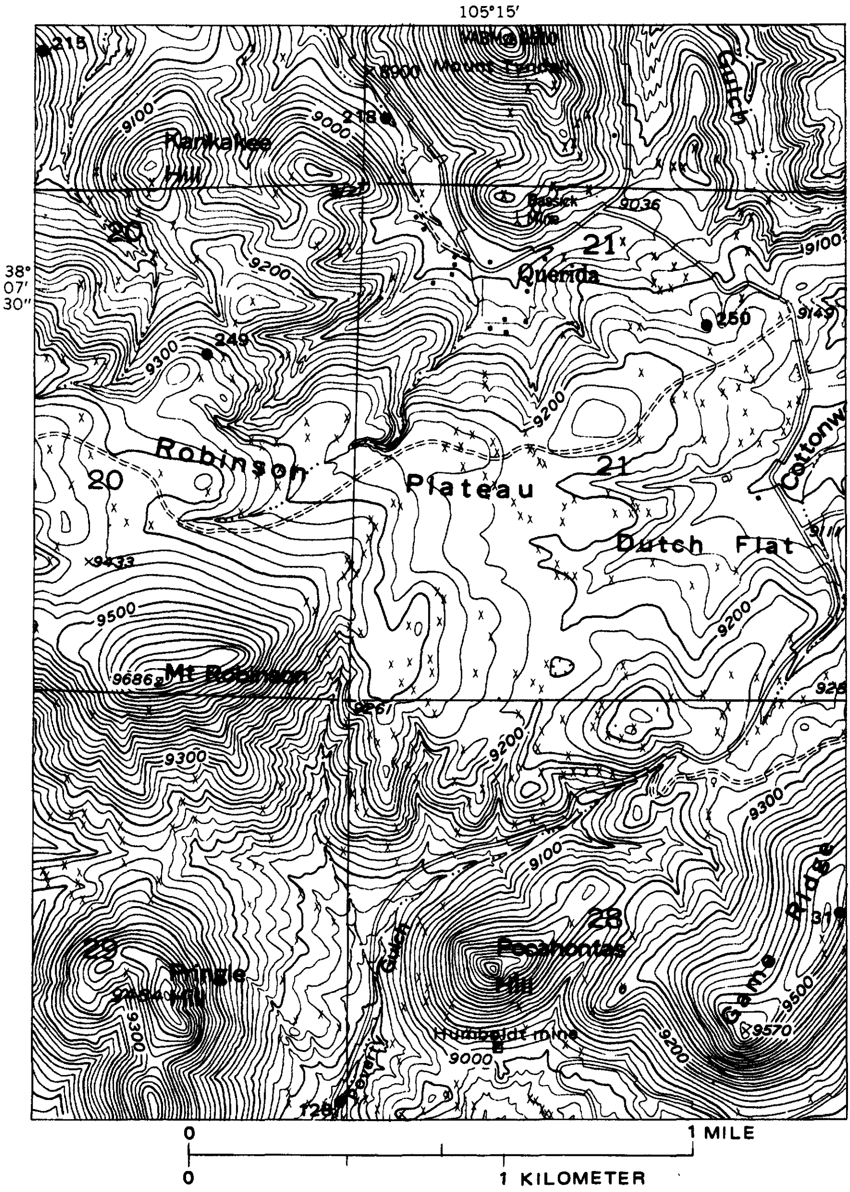

FIGURE 5.—Sample localities in the Rosita area. Mines: 31, Tecumseh; 128, Senator (Maverick); 215, Bunker Hill; 218, Vulcan; 249, Ben Franklin; 250, Maine No. 2.

The first mined ore from the Racine Boy quarry was mostly hand-cobbed bromargyrite,[2] was almost unquestionably free milling, and

[2]Computations based upon 2-year production figures for silver, obtained by raw amalgamation from bromargyrite from the Racine Boy quarry area, which measures about 255 X 500 feet, disclose that about 11.6 tons of bromine was associated with the silver. This large quantity of bromine from such a small area certainly shows that a large volcanic source of bromine was concentrated in this quarry area.

was processed locally by raw amalgamation. As mining progressed and the bromargyrite content decreased, the ores contained relatively more nonamalgamating argentian cryptomelane and were actually a mixture of free-milling and smelter fluxing ores. If the ores were processed by smelting, all the silver was recovered, but if they were processed by amalgamation, only the silver from bromargyrite was recovered, and the argentian cryptomelane passed into the mill tailings. This explains why full recovery of assay values was obtained from those ores shipped and smelted outside the district, whereas only partial recovery of the assay values was obtained if the ores were processed locally by raw amalgamation. Large smelters in the Western United States at that time mixed manganiferous silver ores, which also commanded a premium as a smelter flux, with silver-bearing lead sulfide smelting ores, whereby the manganese fluxed the lead ores, and the lead served to collect the silver from both. We conclude, therefore, that if, instead of amalgamating mills, there had been one first-class smelter of the Argo (Denver) type at or near Silver Cliff, local smelting of all the silver-bearing ores of the district could have been successful, and the district might have prospered longer.

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