

MANGANESE OXIDES FROM THE ARTILLERY
MOUNTAINS AREA, ARIZONA

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ABSTRACT

Psilomelane, hollandite, cryptomelane, coronadite, ramsdellite, pyrolusite and lithiophorite were detected in a microscopic and *x*-ray study of material from four deposits in the Artillery Mountains area. The number of lines present in *x*-ray powder photographs of psilomelane from the area is quite variable. Ramsdellite occurs in both vein and bedded deposits and may have formed under diagenetic conditions in the latter. Soft wadlike material, which comprises the bulk of the manganiferous material in the bedded deposit examined, could not be identified but appears in general to be poorly crystallized, low in barium, high in strontium, and in some respects similar to cryptomelane, hollandite and psilomelane.

The origin of the manganese in the vein deposits studied is not clear, but several features suggest a hypogene origin. Field evidence favors a syngenetic sedimentary origin for the bedded deposit studied.

INTRODUCTION

The manganese deposits of the Artillery Mountains area, southern Mohave County, Arizona, constitute one of the principal low-grade domestic manganese resources. Information on the mineralogy of individual deposits of the area is sparse, perhaps in part due to the fact that much of the manganiferous material is fine-grained and soft, and difficult to study in the laboratory. Subsequent to studies of the geology and deposits of the area Jones and Ransome (1920) and Lasky and Webber (1949) reported psilomelane, pyrolusite and manganite. Havens *et al.* (1947) detected minor braunite in addition to the above oxides, and Rosenbaum *et al.* (1957) indicated that barium and perhaps lead were chemically combined with the manganese oxides. Hewett and Fleischer (1960) postulated the presence of hollandite or psilomelane from chemical analyses.

The present study was undertaken to decipher the manganese mineralogy of a few of the many deposits of the area, and to obtain information on sequences and processes of mineral deposition. Approximately 60 polished sections were examined in detail, and, insofar as possible, optically monomineralic material was carefully removed from them for *x*-ray study. More than 250 *x*-ray powder photographs were taken during the course of the study.

OCCURRENCE

The deposits are of two general types: 1) vein, breccia, fissure, and fault-zone deposits, hereafter called vein deposits, and 2) bedded deposits.

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Three diversely occurring vein deposits, the Black Jack, Price and Priceless, and one bedded deposit, the Plancha, were studied. In addition, a few samples from the large stratiform deposits of the Maggie Canyon area were examined briefly.

The vein deposits studied are composed primarily of numerous veinlets of manganese oxides, generally less than a few inches wide, that occur along fractures, joints, bedding planes, and breccia zones in Tertiary rocks. At places in one vein deposit the manganese minerals are so disseminated that they closely resemble material of the bedded deposits.

Bedded ore¹ appears to be considerably more abundant than vein ore. Known bedded deposits occur principally in the Lower Pliocene(?) Chapin Wash formation, which is composed of former alluvial fan and playa deposits (Lasky and Webber, 1949, p. 14). The bedded ore consists predominantly of soft brown to black wadlike material that cements diverse types of rock. At the Plancha deposit, hard, silvery, blebby layers and patches of manganese oxide, quantitatively unimportant but mineralogically interesting, occur randomly scattered throughout a bed of wadlike material ten or more feet thick. The silvery layers are generally less than 2 inches thick but range up to 20 feet or more in length, and are approximately parallel to the bedding. In the Maggie Canyon area, stratiform deposits contain a substantial tonnage of hard, brown to black, compact to porous ore cut in places by stringers containing one or more of the following: manganese oxides, barite, opal, calcite, clay minerals(?), and very minor fluorite. More detailed accounts of this ore and the soft wadlike material are given by Lasky and Webber.

MINERALOGY OF THE VEIN DEPOSITS

Cryptomelane. Polished surfaces from some portions of the Price deposit contain appreciable amounts of material that give x -ray powder patterns similar to cryptomelane (Table 1). Only minor amounts of cryptomelane were detected in polished sections from the other two vein deposits. Semi-quantitative x -ray spectrographic analyses of two cryptomelane samples show small amounts of barium, strontium, iron, lead and zinc. Very minor arsenic and possible chromium were also detected.

Cryptomelane occurs principally as blades, anhedral grains and needles. In a polished section of ore from the Black Jack deposit, large grains of cryptomelane (Fig. 1) up to 0.9 mm in length were found that in places surround euhedral quartz grains. Some quartz grains are embayed by manganese oxides. Cryptomelane locally embays and cross-cuts large pyrolusite grains in the Price deposit. Soft, black, velvety-appearing

¹ Ore is used in a broad sense to include manganiferous material that is distinguishable with the unaided eye.

TABLE 1. X-RAY DIFFRACTION POWDER PATTERNS OF CRYPTOMELANE, HOLLANDITE, AND CORONADITE

Cryptomelane Price deposit. This study		Cryptomelane W. Australia Faulring <i>et al.</i> , 1960		Hollandite Black Jack deposit. This study		Hollandite Langenberg, Saxony Frondel <i>et al.</i> , 1960		Coronadite Priceless deposit. This study		Coronadite Bou Tazoult, Morocco Frondel and Heinrich, 1942	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
6.96 ¹	80	6.94	S	6.96 ¹	40	6.98	5	6.96 ¹	30		
4.92	80	4.92	S	4.94	10	4.93	3				
3.48	40	3.48	W	3.49	60	3.47	8	3.49	40	3.466	6
3.11	100	3.10	S	3.13	100	3.13	10	3.13	100	3.104	10
2.75	10			2.73	20						
						2.68	1				
								2.51	10		
2.46	40	2.45	W								
2.40	90	2.39	M	2.40	100	2.40	9	2.40	40	2.400	4
2.32	20	2.32	VW								
				2.24	20	2.24	$\frac{1}{2}$				
2.21	40	2.20	W					2.21	40	2.205	4
2.16	70	2.15	M	2.16	90	2.15	8	2.16	30	2.155	2
										2.001	1
1.96	20	1.97	VW	1.97	10	1.98	$\frac{1}{2}$			1.960	1
1.92	30	1.92	W					1.93	10	1.919	1
1.83	70	1.83	M	1.83	30d	1.83	6	1.84	30	1.836	2
1.74	10	1.73	VW			1.74	$\frac{1}{4}$	1.75	10	1.742	1
1.70	10	1.69	VW					1.70	10	1.691	1
1.64	40	1.64	M	1.65	10d	1.65	2	1.65	10d	1.642	2
1.62	20	1.61	VW								
										1.591	1
1.54	70	1.54	M	1.55	40d	1.55	7	1.55	30	1.542	5
1.43	40	1.43	W	1.43	30	1.43	2	1.43	10	1.432	1
1.40	10	1.402	VW					1.40	20	1.400	1
1.37	20	1.39	VVW	1.37	10	1.363	2	1.37	20	1.374	2
1.35	60	1.350	VW					1.36	20	1.356	2
1.30	30	1.297	VW	1.30	10			1.30	10	1.298	1
1.23	30	1.232	VW					1.24	20	1.237	1
1.22	20	1.215	VW					1.22	20	1.218	1
1.20	20	1.193	VW								
1.16	20	1.158	VW								
1.15	10							1.15	10	1.148	1
1.12	20	1.116	VW							1.116	1
1.077	30	1.075	W								

¹ Intensities estimated visually and *d* spacings measured from 114.6 mm powder camera photos. Cryptomelane and coronadite *d* spacings corrected for shrinkage. FeK α radiation and a Mn filter were used for all powder photos of manganese minerals.

coatings in some veinlets consist of numerous, very thin, closely spaced needles of cryptomelane or hollandite oriented with their long axes perpendicular to the velvety surface.

Hollandite. Hollandite appears to be one of the most abundant manganese minerals in polished surfaces from the Black Jack and Priceless deposits. The powder pattern given by a sample from the Black Jack deposit is

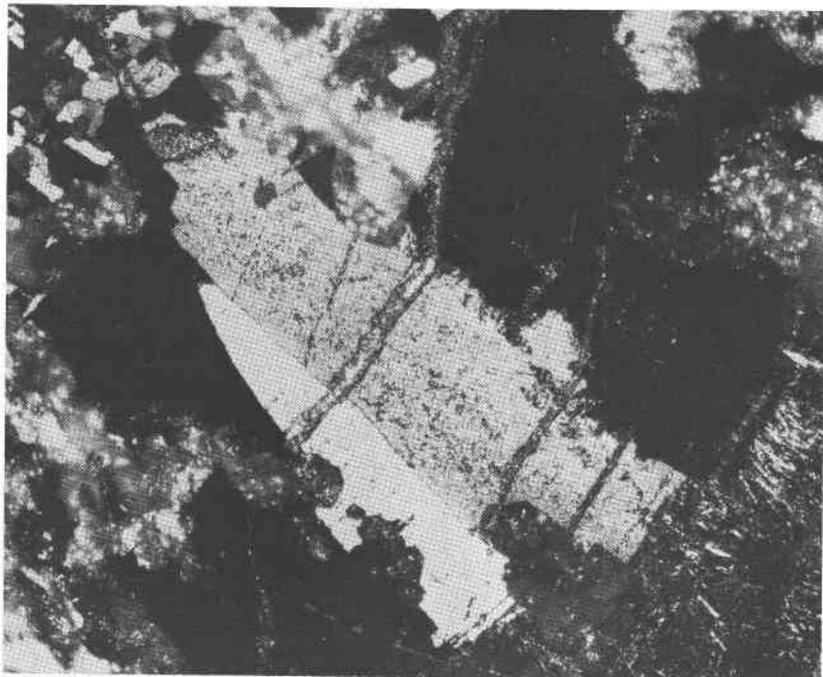


FIG. 1. Photomicrograph. Large cryptomelane grains that occur interlayered with jasper in the Black Jack deposit. The cloudy and unevenly highlighted gray and white material is quartz. Partial outlines of quartz crystals may be seen in places along the edges of the cryptomelane grains. 370X. Crossed nicols.

shown in Table 1. Identical patterns were obtained from samples from the other two deposits. Two confirmatory semi-quantitative x -ray spectrographic analyses of hollandite from the Artillery Mountains area exhibit the same minor elements as cryptomelane but show appreciably higher barium and strontium contents (Fig. 2).

Hollandite occurs as very fine-grained material, as anhedral grains, and as late-formed needles.

Coronadite. One powder pattern (Table 1) obtained from ore from the Priceless deposit shows similarities to published powder patterns of

TABLE 2. X-RAY DIFFRACTION POWDER PATTERNS OF PSILOMELANE AND RAMSDELLITE

Psilomelane Schneeberg, Saxony Gruner, 1943 (From X-Ray Powder Data File)	Psilomelane 1 Priceless deposit. This study		Psilomelane 2 Priceless deposit. This study		Psilomelane Jhabua and Ratanpur deposits India. Mukherjee, 1959		Ramsdellite Price deposit. This study		Ramsdellite Lake Valley, New Mexico Byström, 1949 (From X-Ray Powder Data File)	
	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
		6.9 ¹ 60d	6.96 ¹ 70		6.95	20	4.64 ¹ 10		4.64	20
			5.80 20				4.07 100		4.07	100
			5.55 20				3.23 20		3.24	20
			4.83 20d				3.13 ² 20			
					4.14	10	2.55 60		2.55	100
3.88	30		3.90 20		3.93B	10	2.44 50		2.44	70
3.46	70	3.48 60	3.48 100		3.49	80	2.34 50		2.34	60
3.32	30		3.33 60		3.33B	20			2.32	50
3.24	30	3.24 10d	3.23 60				2.27 10		2.27	10
					3.11	20			2.19	70
			2.99 40		3.02B	15	2.14 ³ 50			
2.88	70		2.89 60		2.86B	15	2.06 20		2.06	40
		2.70 10	2.69 30				1.90 40		1.907	70
					2.66	20	1.83 20		1.828	20
					2.63	5			1.802	10
2.42	70	2.40 100d	2.41 100		2.405	100	1.70 10		1.716	10
2.36	30		2.37 60		2.36	20	1.66 50		1.660	80
					2.315	5	1.62 40		1.621	80
2.26	30	2.25 40	2.26 70		2.25	15	1.54 20		1.541	30
					2.24	40	1.47 40		1.473	80
					2.215	10	1.43 40		1.433	50
2.19	100	2.18 70	2.19 100		2.18	100	1.36 40		1.360	80
2.15	30	2.15 50	2.15 70		2.15	30	1.35 40		1.352	40
					2.13	5			1.337	10
					2.065	10	1.32 20		1.323	50
2.02	10		2.03 10		2.035	15	1.27 10		1.272	60
			1.94 10		1.925	10	1.25 20		1.250	60
			1.86 10		1.865	10			1.219	30
1.82	70	1.82 40d	1.83 50		1.815	50	1.126 10			
			1.74 10		1.735	15	1.072 30			
1.71	10	1.69 10d	1.72 20d		1.71	20				
					1.675	5				
1.64	30	1.64 10d	1.64 20		1.64	25				
1.56	70	1.55 40	1.56 60		1.563	40				
			1.53 10		1.515	10				
1.50	10		1.50 10		1.483	5				
1.42	70	1.42 40	1.43 60		1.425	40				
1.40	70	1.40 10	1.40 50		1.403	25				
					1.375	5				
					1.363	5				
			1.36 10		1.353	10				
					1.340	5				
1.30	10		1.30 10							

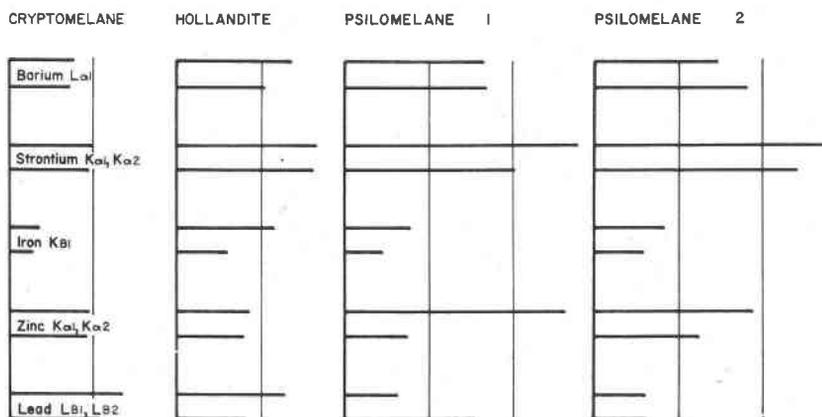


FIG. 2. Semi-quantitative partial x -ray spectrographic analyses. The horizontal lines represent the maximum peak values obtained for a particular spectral line of the element indicated. Two partial analyses of each mineral are given. Distance between vertical lines is equal to one-fourth of the x -ray spectrograph scale. A LiF analyzing crystal was used and all reflections are first order.

coronadite. The powder pattern obtained is nearly identical with a pattern given by material from a U. S. National Museum specimen of coronadite from Morocco (No. 106650).

Psilomelane. X -ray powder photographs were taken of a mineral that is very abundant in polished surfaces from the Black Jack and Priceless deposits. The photos exhibit strong lines that match those published for psilomelane. However, the patterns obtained are of two general types (Table 2) and have been designated psilomelane 1 and psilomelane 2 for convenience. Powder patterns of psilomelane 1 are weak-appearing and diffuse. Lines at approximately 6.9, 3.48, 2.40, 2.25, 2.15, 1.82, 1.55, and 1.42 Å are present in most of the patterns. In sharper patterns additional lines are present. Also, a few lines in diffuse patterns appear to split into two distinct lines in somewhat sharper patterns. The line at approximately 2.40 Å appears as 2.40 and 2.36 Å lines in sharper patterns and that at 2.15 Å appears as 2.18 and 2.15 Å lines. Several patterns that are relatively sharp seem transitional between psilomelane 1 and psilomelane

¹ Intensities estimated visually and d spacings measured from 114.6 mm powder camera photos except for psilomelane 1 which was measured from 57.3 mm powder camera photo. Large camera d spacings corrected for shrinkage.

² Probable pyrolusite line.

³ Several published patterns show a 2.13 Å line of moderate intensity.

2, and it seems possible that psilomelane 1 may be a disordered form of psilomelane 2.

Other patterns obtained have a weak, diffuse 3.10 Å line and a strong 3.47 Å line. These patterns appear transitional between psilomelane 1 and hollandite. In the laboratory, psilomelane heated above 550° C. converts to hollandite (Fleischer and Richmond, 1943) and passes through a period of marked crystal disorder (Wadsley, 1953; Fleischer, 1960) but whether the laboratory data have any bearing on the material investigated by the writer is uncertain.

Patterns of psilomelane 2 are relatively sharp and distinct. Material that gives closely similar patterns occurs at several localities in the Southwest and Mexico.

Mukherjee (1959) and Gruner (1943) have published psilomelane patterns (Table 2) that are somewhat similar to the patterns of psilomelane here reported. The strong 2.88 Å line in Gruner's pattern is missing in the pattern of psilomelane 1 but a diffuse band is present at 2.88 Å in some of the sharper psilomelane 1 patterns. Fleischer (1960) has reported a diffuse psilomelane pattern with lines at 6.87, 3.46, 2.40, 2.18, 2.14, and diffuse bands at 1.82, 1.56, and 1.42 Å, and Neumann and Sellevoll (1955) have reported a pattern somewhat similar to psilomelane 2. Thus, variations in psilomelane patterns are known to exist but causes of variation have apparently not been determined.

Confirmatory semi-quantitative x-ray spectrographic analyses were made of materials which gave psilomelane 1 and psilomelane 2 powder patterns. These analyses, parts of which are shown in Fig. 2, show higher barium and strontium contents than the hollandite samples similarly analyzed. The appreciable strontium content and the sympathetic variation of strontium with barium in cryptomelane, hollandite and psilomelane indicate that strontium is probably present in the structure of these minerals, and perhaps substitutes in the barium or water molecule sites in psilomelane. Possibly strontium in the psilomelane structure may be responsible for some of the differences between powder patterns of psilomelane from the Artillery Mountains area and those of psilomelane published from other areas.

Psilomelane occurs as needles, fine-grained material, and anhedral grains. In several cases layered psilomelane 2 exhibits a felted texture composed of ragged-edged needles or blades.

Ramsdellite. Small tabular to blocky crystals of ramsdellite (Table 2) that range up to 2 mm in length and have a somewhat striated appearance line the centers of a few veinlets in the Price and Priceless deposits. In both deposits ramsdellite follows either hollandite or psilomelane in the para-

genetic sequence. One possible explanation of this sequence is that in the absence of the large cations present in the hollandite structure the double strings composed of oxygen octahedra around manganese ions may be knitted together to a ramsdellite-like arrangement (Byström and Byström, 1950).

Pyrolusite. Pyrolusite occurs sparingly in polished sections from the Black Jack and Priceless deposits. It occurs in appreciable amounts in certain parts of the Price deposit where it is closely associated with cryptomelane. Also, some pyrolusite is present in grains of ramsdellite. It appears to have developed at the expense of ramsdellite, presumably by the Mn ions changing positions (Byström and Byström, 1950).

Lithiophorite. A thin coating of a strongly anisotropic gray mineral that appears to be lithiophorite surrounds ramsdellite grains in one polished surface from the Priceless deposit.

MINERALOGY OF THE BEDDED DEPOSITS

Soft wadlike material. The soft wadlike material of the Plancha bedded deposit could not be identified. X-ray powder patterns indicate that fine-grained silica and other material is intimately associated with the manganese, but none of several different methods of purifying or selectively sampling the soft manganiferous material proved successful. Surfaces of material prepared for examination under the ore microscope would not polish; however, thin sections locally show long, thin, wispy, black needles extending into small openings in the generally amorphous-appearing manganese cement. Somewhat similar-appearing needles of cryptomelane, hollandite and psilomelane were found in several polished sections from the Artillery Mountains area. Semi-quantitative x-ray spectrographic analyses of the material indicate that the same minor elements are present as in the previously mentioned analyses, plus perhaps a very minor amount of rubidium. However, in general, the barium content of the soft wadlike material appears to be quite low and the strontium content appears to be quite high. X-ray powder photos of semi-purified material, one of which is shown in Table 3, have some lines that are present in the patterns of cryptomelane, hollandite and psilomelane. Lines at approximately 6.9 (present in two patterns not shown), 3.46, 2.40, 2.16 and 1.43 Å are present in patterns of all three of the above minerals and lines at approximately 3.23, 2.99, 2.89 and 2.70 Å are present in patterns of psilomelane 2. In summary, the data obtained suggest that the soft manganiferous material in the Plancha deposit is, in general, poorly crystallized, low in barium, high in strontium, and perhaps in some respects similar to cryptomelane, hollandite and psilomelane.

TABLE 3. X-RAY DIFFRACTION POWDER PATTERNS OF SOFT WADLIKE MATERIAL AND LITHIOPHORITE

Soft wadlike material Plancha deposit. This study				Lithiophorite Burro Wash near Price deposit. This study		Lithiophorite Gloucester, South Africa. Wadsley, 1950	
dÅ	I	dÅ	I	dÅ	I	dÅ	I
10 ¹	40	2.16	30b	9.42 ¹	50	9.45	50
6.52	20	² 2.13	30	4.72	100	4.70	100
5.84	20	2.07	10			3.12	35
4.49	20	2.01	20	2.52	10		
² 4.24	60	¹ 1.98	30	2.39	60	2.39	35
4.03	10	1.93	10	1.89	40	1.88	50
3.94	10	1.85	10	1.58	10		
3.77	50	¹ 1.82	30			1.51	20
² 3.66	10	1.80	30	1.47	10	1.46	10
3.46	40	1.70	10			1.45	10
² 3.34	100	¹ 1.67	20	1.40	10	1.40	10
3.23	40	¹ 1.54	40			1.23	20
3.12	10	1.50	30			1.17	10
2.99	50	¹ 1.45	20	1.15	30d	1.15	10
2.89	40	1.43	10				
2.77	30	¹ 1.38	30				
2.70	20	¹ 1.37	30				
2.61	30	1.34	10				
2.57	50	1.31	10				
2.53	10	1.29	20				
² 2.45	20	¹ 1.25	30				
2.40	50vb	¹ 1.23	10				
² 2.28	20	¹ 1.20	30				
² 2.24	20	¹ 1.18	30				

¹ Intensities were estimated visually and *d* spacings were corrected for shrinkage from 114.6 mm powder camera photos.

² Lines attributable wholly or in part to quartz. Sample for x-ray was first sieved through a -200 mesh screen. Some other lines in the pattern may be attributable to mica. Lithiophorite pattern weak because only very small amount of material was available.

Hard silvery ore. The relationships in the hard silvery layers or blebby zones in the Plancha deposit are shown in Fig. 3. Cryptomelane occurs in one or more very thin concretionary rims around individual grains or aggregates of grains of sediment. Ramsdellite grains up to 0.5 mm in length border the free surfaces of the rims and in many instances, as in Fig. 3, fill the remaining space. A number of the ramsdellite grains are partially changed to pyrolusite. Pyrolusite also occurs in the thin concretionary rims. Minor lithiophorite (Table 3) is superimposed on the

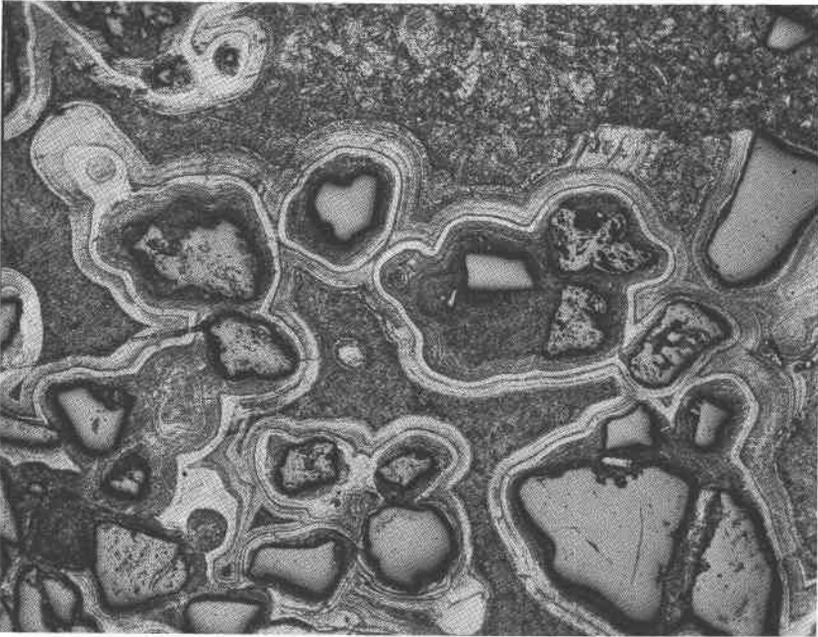


FIG. 3. Photomicrograph. Concretionary thin rims containing cryptomelane and pyrolusite. Ramsdellite-pyrolusite grains of appreciable size are present in the central extreme upper portion of the photo. Small grains of pyrolusite form the outermost rim in the upper portion of the photo. 185X.

hard silvery ore locally and may replace ramsdellite-pyrolusite grains. Minor late-formed acicular cryptomelane is also superimposed on the material of the hard silvery layers.

Hard ore. The hard ore of the Maggie deposits was studied only briefly. Polished surfaces examined contain hollandite, psilomelane and cryptomelane. Some *x*-ray powder patterns obtained are transitional between patterns of cryptomelane and hollandite. The psilomelane patterns obtained are weak-appearing and diffuse and all seem to be psilomelane 1. Several of these patterns have a strong diffuse line at approximately 4.10 Å, the significance of which is uncertain. Ramsdellite and Nsuta MnO₂ both have strong lines in this vicinity and a material structurally similar to cryptomelane but low in potassium has a line at 4.03 Å (Butler and Thirsk, 1952).

ORIGIN

Although cavity filling appears to be the dominant process of ore deposition in the vein deposits studied, the origin of the ore in these

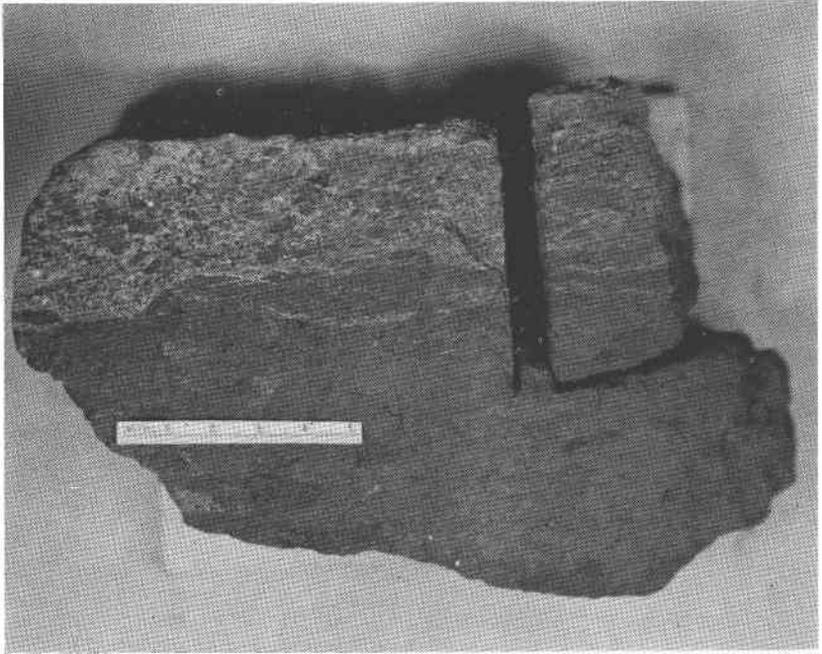


FIG. 4. Contact of black manganiferous bed with overlying barren material. Scale is approximately 5 cm in length.

deposits is not clear. All of the workings in the area appear to be within a few hundred feet of the present surface, and weathering in this desert area may well extend to considerable depths. Ramsdellite, pyrolusite, cryptomelane and lithiophorite occur in one or more of the vein deposits and, as is indicated later, apparently have formed through the action of surface processes in the bedded deposit studied.

However, several features of the vein deposits suggest a hypogene origin. Black calcite and barite-fluorite stringers stained with copper minerals and with vanadinite-mimetite or closely related minerals occur less than a mile away from the deposits. In the case of the Black Jack deposit, barite-fluorite veinlets of similar trend to veinlets in the deposit occur only a few hundred feet away. Volcanic rocks in the area were laid down at various times both prior and subsequent to the deposition of the bedded deposits. Fluorite is present in all three deposits and barite in two. The somewhat generalized paragenetic sequence in polished surfaces from the Black Jack deposit, namely: fluorite and barite, quartz, hematite, manganese oxides, chalcedony and finally calcite, is, in some

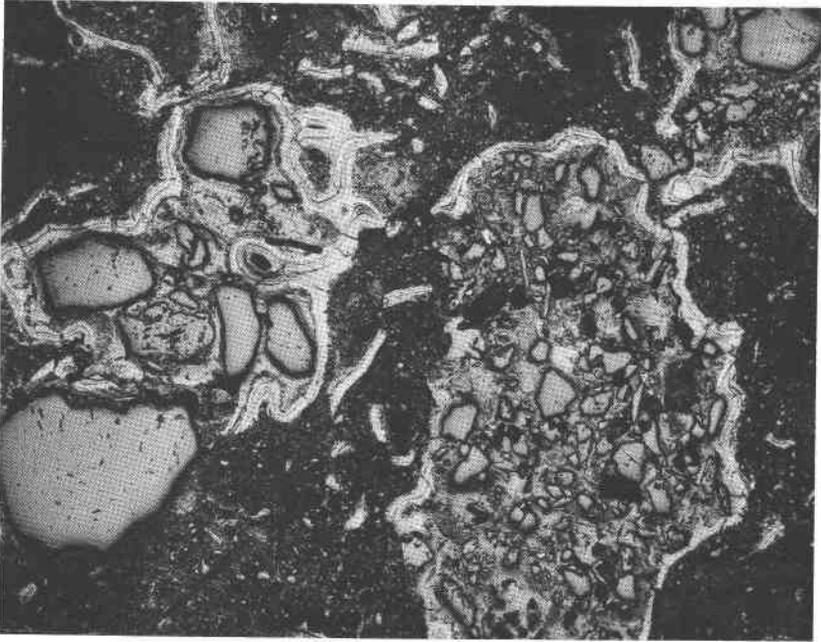


FIG. 5. Photomicrograph. Manganiferous fragments in barren material. Thin concretionary rims of manganese oxide are intact within fragments and broken outside of fragments. 120X.

respects, similar to the quartz, manganese, calcite sequence reported from the hot spring deposits at Golconda, Nevada (Kerr, 1940, p. 1374). The other two vein deposits, one of which appears to contain a blind veinlet, partially duplicate or at least do not seem to contradict this sequence. Barium content appears higher in the Black Jack and Priceless deposits than in the Plancha bedded deposit. One possible explanation is that the barium tends to remain closer to its source because of the relative insolubility of some barium compounds.

Field evidence suggests a syngenetic sedimentary origin for the bedded Plancha deposit. Manganese ore apparently stripped from the top of an ore bed, clastic dikes of barren material extending downward into an ore bed, thinly interlayered barren and manganiferous material, and possible small-scale cross-bedding of barren and manganiferous material are some of the more convincing features of a sedimentary origin. Lasky and Webber, from their study of other deposits in the area, give additional evidence including manganiferous mudflakes.

The silvery ore of the Plancha deposit appears to be diagenetic. In addi-

tion to the field relationships mentioned earlier, a diagenetic origin is also suggested by microscopic relationships. Figure 4 shows a sample from the top of a soft wadlike ore bed in the Plancha deposit. A number of manganese fragments appear to have been stripped from the top of the bed by the influx of the overlying barren material. A polished surface of material taken from the cut in this sample exhibits the relationships shown in Fig. 5. Here, inside fragments of ore stripped from the bed, rims of fine-grained manganese oxide, probably cryptomelane, are intact and surround individual grains or aggregates of grains of sediment. Yet outside these manganese fragments, in the barren material, the rims are broken. Thus, it appears that the rims formed before the influx of the overlying material.

Data obtained from study of the Maggie Canyon area samples is too limited to be set forth in support of a hypothesis of origin. Lasky and Webber attributed the hard ore of these deposits to supergene processes; however, the presence of fluorite and barite in stringers cutting the hard ore suggest that hypogene processes may also have been operative in this zone.

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