

THE CHEMICAL RELATIONSHIP OF CRYPTOMELANE (PSILOMELANE), HOLLANDITE, AND CORONADITE

JOHN W. GRUNER,

University of Minnesota, Minneapolis, Minnesota.

ABSTRACT

The minerals cryptomelane, hollandite, and coronadite are isostructural and form isomorphous mixtures. The unit cell of the group contains 16 O ions. Its formula is:



K, Ba, and Pb occupy identical positions. The ratio of $x:y:z$ is dependent on the state of oxidation of Mn which in turn depends on the conditions under which the mineral forms. H_2O occupies positions which could be filled by K, Ba, or Pb, provided electrostatic balance is maintained. The mineral called originally romanechite by Lacroix has been found to consist of minute crystals of cryptomelane.

INTRODUCTION

Few groups of minerals have caused more confusion for mineralogists and chemists than the manganese oxides. The reasons are either that they resemble one another and give tests which are not sufficiently distinctive for individual species or one is apparently working with a mixture of oxides. Psilomelane heads the list in this respect. Ramsdell (1) in 1932 had shown that "psilomelane" occurs in at least two different structures, one of which is high in Ba, the other contains little or no Ba. Lately he (2) has worked on the unit cell of the Ba-free variety to which Richmond and Fleischer (3) have given the name cryptomelane. The writer was investigating the same minerals when the work of Richmond and Fleischer was published. He was going to propose the name romanechite for this new species for reasons given below.

X-RAY INVESTIGATION

Vaux (4) investigated Ba-psilomelane in 1937 by x -rays and proposed a unit cell and chemical formula. He restricted his work to a few specimens, particularly the material from Schneeberg, Saxony. Unfortunately he did not publish the x -ray spectra and the writer was unable to follow his work until he obtained Schneeberg specimens through the kindness of Dr. Samuel G. Gordon of Philadelphia (see Table 1).

TABLE 1. COMPARISONS OF POWDER SPECTRA
Unfiltered Fe Radiation.
Camera radius 57.3 mm.

Hollandite ¹		Cryptomelane ²		Artificial Compound ³		Psilomelane ⁴	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
6.83	2	6.81	2	6.8	3	3.880	1
4.81	2	4.87	2	4.88	2	3.462	2
3.442	1	3.469	0.5	3.452	0.5	3.320	1
3.077	5	3.084	5	3.077	4	3.239	1
2.467	0.5	2.455	1			2.877	2
2.389	3	2.393	2	2.389	5	2.418	2
2.192	2	2.196	1			2.361	1
2.137	2 <i>d</i>	2.148	1	2.150	1 <i>b</i>	2.255	1
1.939	0.5	1.929	0.5			2.191	3
1.907	0.5					2.150	1
1.820	2 <i>d</i>	1.827	2	1.817	1 <i>b</i>	2.021	0.5
1.622	1	1.637	1 <i>b</i>	1.610	1 <i>b</i>	1.820	2
1.535	3	1.538	3	1.532	2	1.709	0.5
1.432	1	1.428	1	1.428	1	1.635	1
1.353	1	1.353	2 <i>b</i>			1.559	2
1.345	1			1.341	1 <i>b</i>	1.497	0.5
1.300	0.5	1.294	1	1.295	0.5	1.422	2
						1.399	2
						1.296	0.5

b = wide line; *d* = double line.

¹ #8975 U.S. Nat. Museum, Chindwara Dist., India. Contains also some braunite, the lines of which have been omitted.

² Romanèche, Saône et Loire, France, #8137 Museum, Univ. of Minnesota.

³ Reagent from Mallinckrodt. Was amorphous before heating for 24 hours at 500° C.

⁴ Schneeberg, Saxony, #11050, Acad. Natural Sci., Philadelphia, Pa.

Vaux (4, p. 523) states that the psilomelane from Romanèche, Saône et Loire, France, gives the same *x*-ray spectra as the Schneeberg specimens. The same statement is made by Frondel (5, p. 55) in a very recent paper. Since there is no reason for doubting these statements, two varieties of "romanèchite," as it used to be called, must occur at Romanèche, one of them a Ba-psilomelane and the other cryptomelane. There is a specimen at the University of Minnesota which A. Lacroix sent to N. H. Winchell in 1910, labelled romanèchite from Romanèche. Since Lacroix (6, p. 6) himself described the mineral and as this description agrees with the specimen, there can be no doubt but that the material is from Romanèche. It is a beautiful specimen with a botryoidal surface covered completely with needles which are not longer than three-fourths of a millimeter. They are striated, but their terminal faces are too small

for identification. The material under the botryoidal surface is also megascopically crystalline, but needles and massive material are intergrown and matted. Needles as well as the massive material give very good x-ray powder spectra of cryptomelane, as shown in Table 1. The streak of the mineral is almost black. The associated minerals are purple fluorite and white barite.

About six analyses of psilomelane from Romanèche are found in the literature (7 and 8). It is now impossible to correlate them with either one or the other of the two species. So far it has not been possible to obtain an analysis of the specimen described. It contains about 9 per cent BaO and 1 to 2 per cent H₂O. Most of this is not lost below 300°C.

As was already stated by Richmond and Fleischer (3), cryptomelane is a common mineral, more common than Ba-psilomelane. It may contain considerable amounts of Ba as just described, but Ba-psilomelane always contains this element in essential amounts. The x-ray patterns of the cryptomelanes may be quite sharp or they may consist of broad lines, the outer edges of which are difficult to measure. The difference in the quality of the spectra is not any greater than in kaolinites or goethites. Cryptomelane is stable to temperatures near 520°–540°C. The x-ray pattern changes to cubic Mn₂O₃ (bixbyite) above this temperature and to Mn₃O₄ (hausmanite) at a much higher temperature. There is reason to believe that slight differences in composition of cryptomelane have considerable influence on this point of inversion.

Manganese dioxides, or compounds close to MnO₂ in composition, can be obtained as chemical reagents or precipitated in the laboratory. In either case there is no way of predicting whether the material will be essentially amorphous, or pyrolusite, or cryptomelane.

(a) A 20-year-old reagent of Mallinckrodt labeled "MnO₂, Binoxide Pure" is amorphous. When heated to 400°C. for 24 hours it did not crystallize, but above this temperature, and even as high as 525°C., it gave a relatively good pattern of cryptomelane (Table 1). The original material contained much water and some Fe, besides other impurities.

(b) A newly purchased reagent from Mallinckrodt, much purer according to the label, was pyrolusite to start with and did not form cryptomelane before inversion to Mn₂O₃.

(c) The analysis of a reagent from General Chemical Co. after heating 20 hours at 300°C., is given in Table 2. It gave a cryptomelane pattern to begin with and a slightly better one after heating 20 hours at 300°C. If this material is heated to 500°C. for 20 hours, the pattern of Mn₂O₃ (bixbyite) is superimposed on that of cryptomelane. It is thought that all of the material probably would invert if heated a longer period.

TABLE 2. CHEMICAL COMPOSITION OF REAGENT OF "GENERAL CHEMICAL CO." AFTER HEATING 20 HOURS AT 300°C.

(Cryptomelane)		<i>Mol. Ratio</i>
<i>Chemical Composition</i>		
MnO ₂	84.93	.9770
MnO	7.33	.1033
Fe ₂ O ₃	.10	.0006
Na ₂ O	.10	.0016
K ₂ O	3.10	.0329
H ₂ O+	2.22	.1232
H ₂ O-	1.70*	.0943
Analyst—R. B. Ellestad	99.48	

* Water absorbed in less than 24 hours after cooling. The H₂O content as the material comes from the bottle is 16.91%. This is lost as follows:

110°C.	12.62%
300°	15.44
400°	16.10
475°	16.85

The reagent also contains traces of SO₄ and insolubles in HCl.

(d) When KMnO₄ is treated with HCl in a boiling solution and NH₄OH is added in sufficient amounts to keep the solution almost neutral, an amorphous precipitate forms which on heating to 400°C. gives cryptomelane.

(e) When electrolytic Mn (99.9% pure) is dissolved in concentrated HNO₃ and this solution is oxidized with KClO₃ while boiling, the resulting precipitate was pyrolusite in one experiment. In another, amorphous material resulted which on heating to 400°C. gave cryptomelane. These behaviors of precipitated oxides or hydroxides show that the "histories" of the compounds influence the resulting structures.

One of the most interesting findings is that hollandite is isostructural with cryptomelane, as shown by the patterns of Table 1. Since Frondel and Heinrich (5) have shown that hollandite has the same structure as coronadite, an attempt will be made to derive a formula for cryptomelane and hollandite which in turn is based on that of coronadite.

CHEMICAL COMPOSITION

In the earlier attempts to arrive at a formula for psilomelane it was not possible to be sure of the homogeneity of the analyzed specimens. Some of them probably were mixtures. The first analyses checked by x-ray powder spectra are by Vaux (4). He arrives at the following formula for Ba-psilomelane: H₄R₂Mn₅O₂₀, where R stands for Mn²⁺, Ba, Mg,

Ca, Ni, Co, and Cu. Since Mn^{2+} and Ba are each about equal to 1, except in one of his analyses, he could have written the formula also $H_4Mn^2BaMn_3^4O_{20}$. The Ba ion is so much larger than the Mn^{2+} that it probably does not "trade places" with it in the structure. The observed density of this material is in fair agreement with the theoretical content of the unit cell as shown by Vaux.

This does not seem to be the case with coronadite for which Fron- del and Heinrich (5, p. 55) have given the formula $MnPbMn_6O_{14}$ or $MnPbMn_6O_{14} \cdot H_2O$. By their own calculations the content of the unit cell based on the mean of two analyses is, however, $Mn_{.97}Pb_{1.17}Mn_{6.31}O_{15.51}(H_2O)_{.73}$, and the observed density would correspond to this formula. The densities for the two theoretical formulas above would be 4.87 and 4.98, respectively. They are too low by about 10 per cent, which in view of the fact that theoretical densities are usually higher than observed ones, throws doubt on the validity of these formulas. The dimensions of the body-centered pseudotetragonal unit cells are:

Coronadite	$a_0=6.95 \text{ \AA}$	$c_0=5.72 \text{ \AA}$	Volume= 276.2 \AA^3
Hollandite	=6.94	5.71	275.0
Cryptomelane	=9.82	2.86	275.8

The relationship between the two cells is simple: $6.95 \times \sqrt{2} = 9.82$. The horizontal edge of the unit cell of cryptomelane is the same as the diagonal of the base of coronadite. It may be assumed that the distribution of the O ions in the two cells are identical, if not that of all of the atoms or ions. Another significant observation is that the value of c_0 of these cells ($c_0/2$ for coronadite and hollandite) is like c_0 in pyrolusite (polianite). It was pointed out by Vaux (4, p. 526) that Ba-psilomelane has the same c_0 as pyrolusite and that manganite is twice as large (5.74). One is tempted to conclude that these minerals are constructed similarly parallel to the c axis, as is also suggested by their fibers parallel to c .

In Table 3 the three isostructural minerals for which chemical and x -ray analyses are available have been recalculated on the basis that the oxygen content of the unit cell is 16. This number of O ions has been chosen because then the observed densities of the specimens of Table 3 agree best with the theoretical ones. Also, pyrolusite with the same height of unit cell has 16 O ions, provided $a_0=4.38 \text{ \AA}$ is doubled. This comparison can also be extended to manganite which for a unit cell twice as high and a corresponding doubling of its a_0 and b_0 dimensions contains 32 O ions. These facts are too striking as to be without significance.

The hollandite from Balaghat, India, described by Fermor (9, pp. 92 and 93) has been included in Table 3. Though no x -ray spectrogram of this specimen is available, there is little doubt but that it is hollandite.

TABLE 3. CALCULATED ATOMIC CONTENTS AND DENSITIES OF UNIT CELLS BASED ON 16 OXYGENS IN A CELL
Si, Ca, and Mg omitted

	Cryptomelane ¹				Crypt. ³ Artificial	Coronadite ⁵		Hollandite ²	
	1	2	3	4		5	6	Kajli- dongri	Balaghat
Mn ⁴	7.39	7.53	7.16	7.57	7.47	6.72	6.70	6.28	6.78
Mn ²	.22	.42	.37	.26	.79	1.11	.96	.60	1.00
Cu	.01	.04	.01	—					
Co	—	.02	.02	.01					
Zn	.49	—	—	.16			.01		
Al	.05	—	.20	.06		.02	.13	.15	.19
Fe	.05	.02	.38	.01		.07	.13	1.10	.43
Ba	.01	.05	—	—		.01		.95	.15
Sr	—	.02	—	—					
Pb	—	—	—	—					
K	.57	.62	.62	.50	.50				.55
Na	.11	.11	.14	.12	.02				.14
Σ+ ions	8.90	8.83	8.90	8.69	8.78	9.19	9.16	9.08	9.24
Mol. W.	736	734	724	721	730	952	942	830	762
Theor. Density	4.40	4.39	4.33	4.31	4.37	5.68	5.63	4.96	4.56
Sp. Gravity	4.33	4.32	4.41	4.17	n.d.	5.44	5.25 ⁴	4.95	4.59
H ₂ O+	1.10	.71	1.47	1.50	.94— 1.66	.98	.58	none	.48

¹ Chemical analyses and specific gravities of these four in paper by Richmond and Fleischer (3).

² Analyses in Fermor (9, pp. 91 and 93).

³ Artificial cryptomelane of Table 2.

⁴ Low on account of 7% insolubles (Lindgren and Hillebrand).

⁵ Analyses in paper by Frondel and Heinrich (5).

The O of the H₂O of the analyses has been omitted from the 16 O positions in the calculations for the following reasons:

1. Practically all H₂O can be driven off without causing a collapse of the structure. The exact temperature when all H₂O is gone cannot be determined on account of the inversion to Mn₂O₃, at about 500°C. for the material of Table 2.

2. The H₂O₊ content is extremely variable in the three isostructural minerals, approaching zero in hollandite from Kajlidongri. This is shown in the bottom row of Table 3.

3. The artificial cryptomelane of Table 2 absorbs again a part of the water as follows:

After heating to 110°	a trace
After heating to 300°	2.8–3.00%
After heating to 400°	2.3–2.7%
After heating to 475°	2.2%

The rate and amount of absorption differ somewhat depending apparently on the humidity of the atmosphere. It is, however, quite rapid and a matter of only a few hours for the bulk of the H_2O . Natural cryptomelane behaves similarly but much more slowly, depending upon its physical condition. The absorption is only 10 per cent of the total H_2O lost of the specimen from Romanèche. The H_2O content of these crystals is only about 1.2 per cent.

Since this H_2O in a massive specimen (see those of Richmond and Fleischer, 3) cannot be just adsorbed on the surface, one must conclude that it occupies positions large enough for H_2O molecules. It would be like zeolitic water. Positions large enough for K, Ba, and Pb ions would also be able to accommodate H_2O .

At first glance there seems to be no order in the number and distribution of the cations. The sum of them approaches 9 in all of the species. If we arrange them by sizes, we find no agreement either. It has been stated frequently that these minerals are manganates. The Mn^6 ion has a radius of about 0.35 Å while those of Mn^4 , Mn^3 , and Mn^2 are about 0.52, 0.70, and 0.90, respectively. Mn^6 has tetrahedral coordination while the others have an octahedral one. Such ions as Zn, Cu, Co, Al, and Fe can substitute in the octahedral positions. Na could either be octahedral or, as is assumed here, go with K. Since the unit cell of the structure is small, it must be assumed that the number of different atomic positions is small. The complexity of the formula is not a real structural one, but is caused by the numerous possible substitutions. These substitutions, including Mn ions of different sizes, cause distortions in the lattice which prevent the growth of relatively large and distinct crystals. The only direction in which these strains do not hinder growth materially seems to be parallel to the c axis. Fibers are the result in the better developed cryptomelanes and particularly in hollandite and coronadite where higher temperatures may have produced an "annealing" effect.

The ions of Ba, Pb^{++} , and K are of very similar sizes and their substitution, one for another, may be taken for granted. It is, however, strange that only about half as many K ions enter the structure as Pb or Ba ions. The explanation for this behavior must be sought in the state of

oxidation of the Mn. If most of the Mn is present as Mn^4 (as stated commonly in analyses), the 32 negative charges of the structure are practically used up, and K can go into the structure to a very limited extent; "holes" are left. This would be common under oxidizing conditions near the surface of the ground. On the other hand, where considerable Mn is of a lower valence, divalent cations of Ba or Pb, depending upon which are available, could enter the same positions.

A number of experiments were performed to investigate this behavior further. Three portions of the artificial material of Table 2 (heated originally to $300^\circ C$.) were boiled in solutions of $AgNO_3$, $BaCl_2$, and $Pb(NO_3)_2$ for about 24 hours. After many careful washings and drying at $300^\circ C$. for 6 hours, their analyses, converted to oxides, showed the following: 14.68 Ag_2O , 6.01 BaO , 11.84 PbO . If the metals went into the unit cell as ions, they would occupy 1.00, 0.29, and 0.41 positions, respectively. This calculation can be made only if it is assumed that the composition of the cryptomelane remains the same except for the replacement of the K ions by the metals. Analyses for the H_2O^+ and H_2O^- were remarkably similar for the three samples, and much like the original material. In other words, about 3 per cent of H_2O was regained within 3 hours in a steam-heated laboratory. Qualitative tests for K showed that some had gone into solution, some remained in the treated material.¹ The solutions containing the Ag or Pb salts had a pH of about 2.5 and that of Ba, a pH of 4.² Mn was found qualitatively in the first two solutions. The samples treated with Ag or Ba were dark brown in color like the original, that of Pb was very dark gray, practically black. The following conclusions were drawn from these experiments:

Only a part of the K ions is replaced by the new metals. There must be open positions in the structure into which the other metal ions can go. Some ions may be just adsorbed. The fact that Ag is taken up in much larger quantities than Ba or Pb must be partly due to its monovalence, partly possibly to its smaller radius. One other possibility exists, that a part is changed to metallic silver by the action of the Mn^{++} ions. The radius of a silver atom is 1.4 Å. As an atom it would fit into the same positions in which the zeolitic water is stored. There is no doubt, at least in the case of Ba and Pb, that some of the Mn of higher valence must be reduced to a lower state in order to maintain electrostatic balance.

¹ Due to the present emergency no other quantitative work was possible.

² Pyrolusite of extremely fine grain does not show any of these behaviors when treated the same way.

CONCLUSIONS

Cryptomelane, hollandite, and coronadite are isostructural and form isomorphous mixtures to some extent. It is thought that the mixing might be more complete if the solutions from which the minerals form contained the necessary elements in the proper proportions. In other words, if Pb or Ba had been present in considerable concentrations when cryptomelane was forming, these elements could have occupied the K positions, in the structure. The state of oxidation of Mn is important in this connection and controls the ratios $x:y:z$ in the formulas below.

The unit cell of the structure contains 16 O ions. This number gives the best agreement between observed and theoretical densities. There are also structural reasons that suggest this number. The formula which includes all the members of the group is as follows:

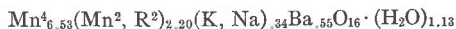


The members could then have the following formulas:

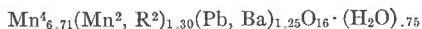
Average of four cryptomelanes of Table 3:



Average of two hollandites of Table 3:



Average of two coronadites:



R^2 includes the elements Cu, Co, Zn, Al, and Fe. The trivalent Al and Fe have been included under R^2 . Allowance must be made for this when x is computed. H_2O given off above 110°C . is present as molecular H_2O filling positions which could be occupied by K, Ba, or Pb, except for electrostatic balance. The total possible amount of H_2O as given in the formulas above is, therefore, determined by the percentage of K, Ba, and Pb in the structure. The actual amount of H_2O comes close to this figure except in hollandite. The water is zeolitic in nature since a part of it at least is reabsorbed after cooling.

Mn designated as Mn^4 in the formula may be partly Mn^6 in which case it would have fourfold coordination and probably occupy different positions from those of Mn of lower valence. It is more likely, however, that all Mn has six coordinates and that its highest chemical valence is 4, as in pyrolusite and other manganese minerals. This would result in a simpler structure which is more likely in the relatively small unit cell. Even then so many substitutions occur in the structures that in most of them considerable strains are set up resulting only in microscopic

crystalline aggregates. The temperatures and pressures of formation have some influence on this behavior. Hollandite, for example, is formed under conditions approaching metamorphism. It is lower in H_2O . Cryptomelane from Romanèche is of hydrothermal origin. Both occur as individual crystals. Cryptomelane can be produced synthetically. This product, as well as natural cryptomelanes, breaks down at about 500° – $540^{\circ}C$. Cubic Mn_2O_3 (bixbyite) is one of the results. The occurrence of a well crystallized cryptomelane, probably the original romanechite of Lacroix, at Romanèche, France, is established.

The writer is indebted to the Graduate School of the University of Minnesota for financial aid and to Dr. R. B. Ellestad for many helpful suggestions.

REFERENCES

1. RAMSDELL, L. S., *Am. Mineral.*, **17**, 143 (1932).
2. RAMSDELL, L. S., *Am. Mineral.*, **27**, 611 (1942).
3. RICHMOND, W. E., AND FLEISCHER, MICHAEL, *Am. Mineral.*, **27**, 607 (1942).
4. VAUX, GEORGE, *Mineral. Mag.*, **24**, 521 (1937).
5. FRONDEL, C., AND HEINRICH, E. W., *Am. Mineral.*, **27**, 48 (1942).
6. LACROIX, A., *Mineralogie de la France*, **4**, 6 (1910).
7. GORGEU, A., *Bull. soc. franc. min.*, **13**, 21 (1890).
8. ZAMBONINI, F., AND CAGLIOTI, V., *Compt. rend. acad. sci., Paris*, **192**, 750 (1931).
9. FERMOR, L. L., *Mem. Geol. Surv. India*, **37** (1909).