THE CRYSTAL STRUCTURE OF CRYPTOMELANE

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Abstract

A crystalline specimen of cryptomelane, examined on a Weissenberg goniometer, is shown to be monoclinic with cell dimensions, $a=9.79$ Å, $b=2.88_6$ Å, $c=9.94$ Å, and $\beta=90°37'$, the space group being $Im(C_s^3)$ or $I2/m(C_{2h}^3)$. The formula KR_8O_{16}, R being mainly Mn^{4+}, corresponds well with chemical analysis.

Cryptomelane, a commonly occurring potassium manganese dioxide, was first identified as a distinct species by Ramsdell in his study of the manganese minerals (1). Although it may vary somewhat in composition, a formula KR_8O_{16} has been suggested (2), where R is mainly Mn^{4+} which is replaced to some extent by other metals, notably copper, zinc, cobalt, and Mn^{2+}. Crystalline occurrences are rare, but Weissenberg photographs taken on a cleavage specimen (3) and on fibrous needles (4) have given evidence of a body-centred tetragonal unit cell of dimensions: $a=9.82$ Å, $c=2.86$ Å. This conformed with both powder and fibre photographs (4).

We have recently examined a crystalline specimen (No. 4199) which was received from the Geological Survey of India by the courtesy of the Director, Dr. W. D. West. This was obtained from the Manganese Mine, Sitapar, Chhindwara District, Central Provinces and labelled hollandite. As the specimen contains 2.5% barium and 5% potassium and its powder diffraction pattern differs slightly from that of hollandite, it is considered to be cryptomelane. Fleischer and Richmond report the presence of cryptomelane in this area (2). It is now thought that cryptomelane and hollandite are isostructural (3, 5) and the barium is most probably present as an isomorphous replacement of the potassium.

The cryptomelane was composed of a matrix of small crystals up to 2 mm. in length, showing at least one good cleavage face, interspersed with parallel groups of crystals which had a tabular appearance, approximately 1 cm. square. Some haematite could be noted in a polished section. Specimens of the two types of crystals gave identical powder patterns which differed in detail from that of previous samples of cryptomelane (2). Many reflections, reported by Fleischer and Richmond as single, are resolved into doublets and triplets. The spacings derived from the proposed unit cell do not account for these and it would appear that the symmetry is lower than tetragonal. Comparison of the powder patterns for the Sitapar specimen with local massive cryptomelane samples suggests that the small crystallite size of the massive mineral causes sufficient line broadening to obscure its lower symmetry. Difficulty was experienced in obtaining suitable crystals and even those which were selected for study were twinned. One crystal is related to its twin by a rotation of 90° and it is probable that the twinning occurs on the (100) and (001) faces, respectively. The twinning and close approximation to tetragonal symmetry indicate a similarity in the atomic distribution parallel to these faces. On zero-layer moving films taken on a Weissenberg goniometer (6), accurate spacings were measured and the symmetry established as monoclinic. The dimensions are $a = 9.79$ Å, $b = 2.88_6$ Å, $c = 9.94$ Å and $\beta = 90°37'$. Volume of the unit cell = 280.7 Å^3. The angle β was derived by triangulation using the spacings d_{100}, d_{101} and d_{101}. The radiation used was Fe Kα ($\lambda = 1.937$ Å). Indexing of moving films of $\{hk0\}$, $\{0kl\}$, $\{h0l\}$ and $\{h1l\}$ zones shows that reflections appear only when $h+k+l = 2n$; the cell is body-centered and the space group Im or $I2/m$.

TABLE 1. ANALYSIS AND CELL CONTENTS OF CRYPTOMELANE (Sitapar)

		Unit cell contents (O=16)		
MnO_2	79.94%	Mn^{4+}	6.99	6.99
MnO	6.09	Mn^{2+}	0.65	1.01
Al_2O_3	0.98	Al	0.15	
MgO	0.16	Mg	0.03	
Na_2O	0.74	Na	0.18	
BaO	2.76	Ba	0.14	1.10
K_2O	5.95	K	0.96	
$H_2O + 120°$ C.	0.36			
$H_2O - 120°$ C.	0.00			
Fe_2O_3	3.42			
Total	100.40			
Density (obs.)	4.35	Density (calc.)		4.33

Absent: SiO_2, CaO, ZnO, CoO, WO_3 and P_2O_5.

The alkali contents were determined by Mr. C. E. S. Davis using the flame photometer.

The chemical composition and computations to determine the contents of the unit cell are given in Table 1. For this purpose it is assumed that manganese may assume the valencies 4 and 2 and that all the Fe_2O_3 is present as a separate constituent.

The best formula which can be given is $KRMn_7O_{16}$, in which barium replaces potassium in the ratio 1:6. Gruner has suggested that sodium may replace potassium (5), but the disparity in the ionic sizes has led to inclusion in R where R is Mn^{2+}, Al, Na and Mg. Since the fomula corresponds to the contents of a body-centred unit cell, the formula for the equivalent group is $K_{\frac{1}{2}}R_4O_8$ (R being mainly Mn^{4+}). It would appear that only half of the potassium sites are occupied and no simple formula, e.g., $K_2Mn_8O_{17}$, containing two K ions per unit cell (as the limiting case) is compatible with the space group data, unless a certain proportion of Mn^{4+} passes to a lower valency state in order to maintain ionic balance. The potassium ions must be distributed throughout the structure in a random manner. The amount of potassium is not fixed and should be variable over a wide range without modification of the structure. Powder diffraction data from a laboratory preparation which was potassium free agree closely with that for cryptomelane, supporting this conjecture. The recorded analyses of cryptomelane (3) indicate that the potassium content does vary over a wide range. It suggests that this mineral is formed as a manganese dioxide mineral with intrusion of potassium ions, a sufficient change from Mn^{4+} to Mn^{3+} or Mn^{2+} occurring to preserve cationic balance. Some substitution by other metals for these lower valence ions may then occur.

A more detailed structure analysis of the Sitapar specimen is being carried out.

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References

1. Ramsdell, L. S., An x-ray study of psilomelane and wad: *Am. Mineral.* **17,** 143 (1932).
2. Fleischer, M., and Richmond, W. E., The manganese oxide minerals: a preliminary report. *Econ. Geol.*, **38,** 269 (1943).
3. Richmond, W. E., and Fleischer, M., Cryptomelane, a new name for the commonest of the psilomelane minerals: *Am. Mineral.*, **27,** 607 (1942).
4. Ramsdell, L. S., The unit cell of cryptomelane: *Am. Mineral.*, **27,** 611 (1942).
5. Gruner, J. W., The chemical relationship of cryptomelane, hollandite and coronadite: *Am. Mineral.*, **28,** 497 (1943).
6. Mathieson, A. McL., Design for an equi-inclination Weissenberg goniometer. (To be published.)