THE UNIT CELL OF CRYPTOMELANE

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ABSTRACT

Weissenberg and powder photograph data obtained from a specimen labelled "psilomelane," from Nassau, Germany, indicate a body-centered tetragonal lattice, with $a_0=9.82$Å., $c_0=2.86$Å, and $c/a=0.29$. The specimen gives a negative test for barium, and conforms to the material designated as cryptomelane by Richmond and Fleischer.

In 1932 the writer reported the result of an x-ray study of a large number of specimens of so-called psilomelane.[1] On the basis of powder photographs it was established that some of the material was actually pyrolusite, or in a few cases, braunite. The remainder of the specimens gave powder patterns indicating that at least three distinct structural types were present. The type which occurred much more frequently than the other two was arbitrarily called "true" psilomelane. A second type included those specimens containing an appreciable amount of barium. Among these was a specimen from Romanèche, France. Specimens labelled "psilomelane, var. lithiophorite" made up the third type.

In 1936 Vaux[2] made an x-ray study of pyrolusite and psilomelane, using the name psilomelane for the material containing barium. Although he did not publish the measurements of the powder pattern, his specimens included one from Romanèche, so it is probable that they correspond to the second type referred to above. Vaux established the identity of this Romanèche material with Haidinger's original psilomelane from Schneeberg, and rightly calls it psilomelane. Vaux had material sufficiently well crystallized to make single crystal as well as powder photographs, and was able to determine the unit cell. It is orthorhombic, with $a_0=9.1$, $b_0=13.7$ and $c_0=2.86$Å.

In the writer's original report he described a specimen from Nassau, Germany. This gave a pattern corresponding to his first type, and was unusual in that individual needles projected several millimeters from the surface of radial fibrous groups. The data here presented have been secured from this specimen. Rotation photographs were obtained from the needles, and show well defined zero and first layer lines. From the layer line spacing, the identity period along the needle axis, considered to be the c axis, is 2.86Å, corresponding exactly with Vaux's value for psilomelane.

The first attempts to obtain Weissenberg photographs showed that the

[1] *Am. Mineral.*, **17**, 143–149 (1932).
[2] *Mineral. Mag.* **24**, 521–526 (1937).

needles are not individual crystals, but rather bundles of smaller fibers with more or less random orientation about the needle axis. A few needles were selected which gave some evidence of crystal faces. These were about 0.1 mm. in diameter. The faces were curved, and gave reflections over quite an angular range. After several trials, one needle was found which had sufficient parallelism of the fibers to give very crude Weissenberg photographs. The reflections are weak, few in number, and in some cases are spread over a range of 10 to 20°. However, there appears to be a definite repetition of the pattern every 90°, thus indicating four-fold symmetry. Moreover, a careful comparison of the zero and first level photographs indicates quite definitely a body-centered lattice. A value of $a_0 = 9.82$Å was obtained from the zero level film. This could be measured with considerable accuracy, for the spots are spread out only in a direction at right angles to the direction of measurement.

These needles, therefore, are body-centered tetragonal, with $a_0 = 9.82$Å and $c_0 = 2.86$Å. This gives an axial ratio of 0.29, which is in agreement with the general rule that needle-like crystals have small axial ratios. With these values for the dimensions of the unit cell, the powder photographs could be completely indexed, and the only reflections present are those with $h+k+l=2n$, which is characteristic of a body-centered lattice. This confirmation from the powder photographs gives additional support to the Weissenberg data.

Two types of powder photographs were made, one in the usual manner from powdered material, and one from uncrushed fibers in a capillary tube. The latter, because of the preferred orientation of the *c* axes, show no *hkl* reflections, but emphasize the *hk*0 reflections, and thus had the advantage of revealing some *hk*0 reflections that were too weak to be detected on the films obtained from the powdered material. Table 1 records the film measurements, with the assigned indices and calculated spacings.

If the material in which barium is an essential constituent is called psilomelane, then this barium-free material, being both chemically and structurally different, represents a distinct mineral species. Its physical properties overlap those of psilomelane, but the *x*-ray data definitely distinguish the two.

Richmond and Fleischer[3] have made a study of the so-called psilomelanes, including chemical analyses, and for this structural type, containing little or no barium, have proposed the name cryptomelane.

[3] See this issue, page 607.

TABLE 1. POWDER PHOTOGRAPH DATA FOR CRYPTOMELANE

Reflecting planes *hkl*	Calculated spacings Å	Fibers		Powder	
		Observed spacings Å	Observed intensity	Observed spacings Å	Observed intensity
110	6.94	6.92	m	6.92	w
200	4.91	4.91	m	4.91	w
220	3.47	3.47	m	3.47	vw
130	3.105	3.11	vs	3.11	m
400	2.455	2.46	m	2.46	vw
121	2.395			2.40	s
330	2.31	2.325	w		
240	2.195	2.205	ms	2.21	w
301	2.15			2.16	w
150	1.925	1.935	m		
141	1.83			1.835	m
440	1.735	1.74	w		
350	1.685	1.69	w		
600	1.635	1.64	s	1.64	w
260	1.55	1.55	w		
251	1.54			1.54	m
002	1.43			1.43	w
170 550	1.39	1.40	vw		
460	1.36	1.36	w		
451	1.36			1.35	m
370	1.29	1.295	ms	1.295	w
402	1.235			1.24	vw
332	1.215			1.22	vw
660	1.155	1.16	w		
561 152	1.15			1.15	w
190	1.085	1.09	vw		
390	1.035	1.04	vvw		
4.10.0	0.91	0.92	vvw		
880	0.87	0.87	w		

The spacings given are the average of measurements made on two films, one taken on a G.E. diffraction outfit, with $Mo_{K\alpha}$ radiation, the other on a smaller camera, with $Cu_{K\alpha}$ radiation.