

*Priderite, a new mineral from the leucite-lamproites of the west Kimberley area, Western Australia.*

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*Introduction.*

DURING an analysis by X-ray diffraction techniques of some fine-grained leucite-lamproites from the west Kimberley area of Western Australia the author became interested in the rutile in these rocks. Although rutile had been repeatedly observed under the microscope (1, 2), its presence could not be confirmed using X-ray diffraction methods. At the author's request, Professor R. T. Prider supplied a small amount of the mineral which had been identified as rutile. A study of this mineral showed it to be a new mineral similar to rutile in its optical properties.

Priderite is the name suggested for this mineral. Rex Tregilgas Prider, Professor of Geology at the University of Western Australia, has contributed much to the knowledge of Western Australian rocks and minerals, and in particular he has studied in detail the suite of rocks from which this mineral was separated.

*General description.*

A mineral similar to rutile in its properties is a constant accessory in all the leucite-bearing rocks of the west Kimberley district of Western Australia (1, p. 50). This mineral has, in earlier papers, been referred to as rutile. In the finer-grained lamproites (fitzroyite, cedricite, and mamilite) it occurs as minute reddish rods of the order of 0.05 mm. long, but in the coarser wolgidites (1, pp. 53 and 58) it occurs as stout prisms measuring up to  $1 \times 0.5$  mm. These 'rutile' prisms exhibit a peculiar lamellation parallel to the base, and in the rocks from Wolgidee Hills this is seen to be due to the crystals being built up of 'rhombic-shaped plates' (1, p. 58). This so-called 'rutile' was separated from the Wolgidee Hills type specimen of wolgidite (which also yielded the two other new minerals, wadeite and magnophorite, described by Prider (2)) for chemical and X-ray work. An examination of this material in oils

reveals that when crushed it breaks into extremely thin nearly rectangular cleavage flakes—the ‘rhombic shape’ of the flakes mentioned by Wade and Prider (1, p. 58) being due to the fact that the sections in which they were seen were cut somewhat obliquely to the base. This mineral has been re-examined by R. T. Prider and the characteristics are as follows:

Habit: rectangular prisms with a lamellation parallel to the base.

Cleavage: basal highly perfect, and fair parallel to the prism, so that it breaks into extremely thin rectangular plates.

Colour: black with adamantine lustre (similar to nigrine); streak, grey.

Optical characters: very thin basal plates are yellowish-brown and show the emergence of the optic axis normal to the cleavage; uniaxial with positive sign; very high refractive index,  $\omega$  greater than 2.10.

Does not fluoresce in ultra-violet light of wave-length 2537 Å. With these characters the mineral therefore resembles rutile very closely.

Pleochroism: in thin section it is deep reddish-brown with  $\omega$  reddish-brown,  $\epsilon$  deep reddish-brown to black.

The crystal fragments used in the X-ray study were 0.1–0.3 mm. in their greatest dimension. They were weakly attracted by an electromagnet indicating that they are paramagnetic. The density determined on 0.2 gram of priderite using a microopyknometer similar to that described by Winchell (3) gave a value of  $3.86 \pm 0.08$  g./cm.<sup>3</sup> Priderite was unchanged, as judged by its X-ray diffractions pattern, after heating to 1400° C.

The result of a chemical analysis made on a sample of 0.15 gram of priderite is shown in table I.

TABLE I. Chemical analysis of priderite.

SiO <sub>2</sub>	...	...	0.0	Unit-cell contents.		
TiO <sub>2</sub>	...	...	70.6	Ti <sup>4+</sup>	...	6.48
Fe <sub>2</sub> O <sub>3</sub>	...	...	12.4	Fe <sup>3+</sup>	...	1.14
Al <sub>2</sub> O <sub>3</sub>	...	...	2.3	Al <sup>3+</sup>	...	0.33
BaO	...	...	6.7	Ba <sup>2+</sup>	...	0.32
K <sub>2</sub> O	...	...	5.6	K <sup>+</sup>	...	0.87
Na <sub>2</sub> O	...	...	0.6	Na <sup>+</sup>	...	0.14
CaO	...	...	trace	O	...	16
MgO	...	...	0.0			

98.2

The analysis was performed by the Assay Department of the School of Mines, South Australia, and J. D. Hayton of the Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization.

TABLE II. Powder diffraction patterns of priderite, Ba-priderite, and cryptomelane.

		Priderite		Ba-priderite		Cryptomelane <sup>1</sup>	
$d/n$ (obs.) $kX$ .	$I$ .	$hkl$ .	$d/n$ (calc.)	$d/n$ (obs.) $kX$ .	$I$ .	$d/n$ (obs.) Å.	$I$ .
7.13	m	110	7.135	7.12	vw.d	6.92	w
5.04	m	200	5.045	5.06	w	4.91	w
3.57	vw	220	3.567	3.55	w	3.47	vw
3.19	s	310	3.190	3.19	s	3.11	m
2.845	vw	101	2.841	2.817	vw	—	—
2.527	vw	400	2.523	—	—	2.46	vw
2.470	m	211	2.475	2.470	m-s	2.40	s
2.379	vw	330	2.378	—	—	2.325	(w)
2.258	vw	420	2.256	2.250	vw	2.21	w
2.222	w	301	2.222	2.223	m	2.16	w
2.034	vw	321	2.034	2.032	vw	—	—
1.981	vw	510	1.979	1.977	vw	1.935	(m)
1.887	m	411	1.886	1.884	w-m	1.835	m
1.787	vw	440	1.783	—	—	1.74	(w)
1.737	vw	530	1.730	—	—	1.69	(w)
1.684	w	600	1.682	1.683	m	1.64	w
1.585	w-m	{ 620	1.595	1.583	w-m	{ 1.55	(w)
		{ 521	1.579			{ 1.54	m
1.480	w	{ 002	1.480	1.475	vw	{ 1.43	w
1.450	vw	{ 112	1.449	1.446	vw	—	—
		{ 611	1.447			—	—
		550	—	—	—	1.40	(vw)
1.421	vw	202	1.420	1.415	vw	—	—
1.394	w	{ 640	1.399	1.390	w-m	{ 1.36	(w)
		{ 541	1.391			{ 1.35	m
1.370	vw	222	1.367	—	—	—	—
1.343	vw	{ 312	1.343	1.340	w	—	—
		{ 631	1.341			—	—
1.327	vw	730	1.325	1.323	vw	1.295	w
1.295	vw	701	1.296	—	—	—	—
1.277	vw	402	1.277	—	—	1.24	vw
1.257	vw	{ 332	1.257	—	—	1.22	vw
		{ 721	1.255			—	—
1.238	vw	422	1.237	—	—	—	—
1.190	vw	600	1.189	—	—	—	—
		{ 651	—	—	—	1.16	(w)
		512	—	—	—	—	—
1.176	vw	750	1.173	—	—	—	—
1.156	vw	811	1.153	—	—	—	—
1.138	vw	442	1.139	—	—	—	—
1.116	vw	910	1.114	1.113	w	1.09	(vw)
1.110	vw	602	1.111	—	—	—	—
1.099	vw	831	1.103	—	—	—	—
1.086	vw	622	1.085	—	—	—	—
1.067	vw	930	1.063	—	—	1.04	(vw)
1.028	w	712	1.027	1.026	vw	—	—
1.019	vw	{ 770	1.019	—	—	—	—
		{ 642	1.017			—	—
1.009	vw	10.0.0	1.009	1.007	vw	—	—
0.9897	vw	10.2.0	0.9894	—	—	—	—
0.9627	vw	213	0.9639	—	—	—	—
0.9459	vw	303	0.9469	—	—	—	—
		10.4.0	—	—	—	0.92	(vw)
0.9285	vw	{ 323	0.9305	—	—	—	—
		{ 662	0.9270			—	—
0.9195	vw	752	0.9193	—	—	—	—
0.9151	vw	413	0.9151	—	—	—	—
0.9133	vw	11.1.0	0.9135	—	—	—	—
0.8907	vw	{ 880	0.8918	—	—	0.87	(w)
		{ 912	0.8902			—	—
0.8867	vw	503	0.8864	0.886	w.d.	—	—
0.8730	vw	523	0.8730	0.873	w	—	—
0.8650	w	10.4.0	0.8652	0.864	vw	—	—
0.8479	vw	613	0.8480	—	—	—	—
0.8359	w	543	0.8363	—	—	—	—
0.8298	vw	12.2.0	0.8294	—	—	—	—

Visual estimate of intensity: s strong, m medium, w weak, v very, d diffuse.

<sup>1</sup> Cryptomelane from L. S. Ramsdell (6) in Å. units; lines in parentheses occurred only on a fibre photograph.

*Diffraction studies.*

X-ray powder diffraction patterns were obtained using two cameras having diameters of 5.73 and 19 cm. The powder specimen was 0.3 mm. in diameter and gum tragacanth was mixed with the powdered priderite to reduce absorption errors. Exposures were made using filtered copper radiation. A list of interplanar spacings and line intensities is given in table II.

Using the method of Hesse (4), indices were assigned to the spacings and the unit-cell dimensions were determined. The dimensions were found accurately by using the 19-cm. camera and measuring the lines of priderite relative to those of sodium chloride; the latter was included in the specimen as an internal standard. Measurements were made in the back reflection region where the  $\alpha_1$  and  $\alpha_2$  lines were resolved.

The unit cell was found to be body-centred tetragonal with the dimensions:  $a$   $10.11 \pm 0.02$  Å. ( $= 10.09$   $kX$ ),  $c$   $2.964 \pm 0.004$  Å. ( $= 2.958$   $kX$ ). This unit cell has since been confirmed by A. D. Wadsley,<sup>1</sup> who has obtained zero and first-level Weissenberg photographs about the  $a$ - and  $c$ - axes of a crystal.

*Discussion.*

During this study the close resemblance between the diffraction patterns of priderite and cryptomelane was noticed. For comparison the main lines of cryptomelane from data by Ramsdell (6) are recorded in table II. Cryptomelane has a body-centred monoclinic (pseudo-tetragonal) cell (5-8) with  $a$  9.79,  $b$  2.88,  $c$  9.94 Å.,  $\beta$   $90^\circ 37'$ . The formula of cryptomelane approximates to  $KR_8O_{16}$  where R is mainly  $Mn^{4+}$ .

The  $c$ -axes of priderite and rutile are almost the same, while the  $a$ -axis of priderite is approximately twice that of rutile. If the density of packing of the oxygen atoms in the two minerals is assumed to be approximately the same (9), then priderite will contain four times as many oxygen atoms as the unit cell of rutile. Table I shows the contents of a unit cell of priderite taking as a basis 16 oxygen atoms. The density of priderite, calculated from the contents and dimensions of a unit cell is 3.948 g./cm.<sup>3</sup> This is in reasonable agreement with the experimental value of  $3.86 \pm 0.08$  g./cm.<sup>3</sup>

Because of their similar radii it is assumed, in table I, that the ions  $Ti^{4+}$ ,  $Fe^{3+}$ , and  $Al^{3+}$  occupy one set of positions in the unit cell, while

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$K^+$  and  $Ba^{2+}$  occupy another set of positions. The position of the  $Na^+$  ion is doubtful because its radius is between the radii of  $Ti^{4+}$  and  $K^+$ .

The formula of priderite is approximately  $(K,Ba)_{1.33}(Ti,Fe)_8O_{16}$ . The ratio of  $(K+Ba)$  to  $(Ti+Fe)$  is 1:6, an integral relationship which is regarded as purely fortuitous. Since a perfect body-centred unit cell must contain at least two of any one atom, priderite must have a defect structure. Assuming that the structure of priderite is similar to that of cryptomelane its formula may be written as  $A_{2-y}B_{8-z}O_{16}$  (7) where  $A$  are the large ions  $K^+$  and  $Ba^{2+}$  and  $B$  are the smaller ions  $Ti^{4+}$ ,  $Fe^{3+}$ , and  $Al^{3+}$ ;  $y$  is of the order of unity, while  $z$  is very small.

Priderite has been synthesized by several methods. It was prepared by fusing a powdered mixture of  $TiO_2$  and  $K_2CO_3$  or  $TiO_2$  and  $BaCO_3$  in an oxyacetylene flame. The minerals prepared in this way usually contained a small rutile impurity, so that their  $K_2O$  and  $BaO$  contents were uncertain. However, diffraction patterns of synthetic K-priderite with different  $K_2O$  contents were identical with that of the natural mineral. The diffraction pattern of Ba-priderite is recorded in table II and although not identical with that of the natural mineral it indicates that, superficially at least, they are isostructural. The K-priderite was also synthesized by heating to  $1000^\circ C.$  an intimate mixture of  $KF$  and  $TiF_4$ .

Hollandite and cryptomelane are considered to be members of an isostructural series (5, 7, 9). K-priderite and Ba-priderite appear to be members of an analogous series. Although the structure of priderite has not been determined, all the evidence indicates that it is similar to that of the cryptomelane series (7). A. D. Wadsley is at present carrying out a structure determination on priderite.

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*Abstract.*—Priderite is the name suggested for a new mineral with the formula  $(K,Ba)_{1.33}(Ti,Fe)_8O_{16}$ . X-ray diffraction studies show that the

mineral is body-centred tetragonal with  $a$  10.11,  $c$  2.96 Å. Structurally the mineral resembles cryptomelane,  $\text{KMn}_8\text{O}_{16}$ , the Ti of priderite being equivalent to the Mn of cryptomelane. Synthetic K- and Ba-priderites appear to be isostructural and they are probably members of a series analogous to cryptomelane-hollandite.

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