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Minyulite (hydrous K-Al fluophosphate) from South Australia.

By L. J. SPENCER, F. A. BANNISTER, M. H. HEY,
and Miss HILDA BENNETT.

Mineral Department of the British Museum.

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IN 1908, at the close of the Franco-British Exhibition at Shepherd's Bush, London, a series of rock phosphates from various localities in South Australia was transferred to the Mineral Department of the British Museum as a present from the Government of South Australia. One large block from Wait's quarry at Noarlunga,¹ 20 miles south of Adelaide, showed cavities lined with crusts of minute crystals. These crystals were determined goniometrically and optically in 1908 to be orthorhombic, and qualitative chemical tests showed the presence of Al, Mg, P, F, and H₂O (K was missed). This evidently represented a new mineral, and it is only now that the work has been successfully completed by the three junior authors. In the meantime, however, the same mineral was discovered in Western Australia by the late Dr. E. S. Simpson² in 1932, and named minyulite, from Minyulo Well. This he determined optically to be orthorhombic, and the formula was given as $KAl_2(OH,F)(PO_4)_2 \cdot 3\frac{1}{2}H_2O$ or $2K(OH,F) \cdot 4AlPO_4 \cdot 7H_2O$. Crystallographic and X-ray data are now given for this species.

The large block (no. 18) was broken up and several hand-specimens (B.M. 1909,53) were retained for the collection. Lining small cavities and filling veinlets in the compact buff-coloured rock phosphate is a thin layer of opaque white apatite with a finely fibrous structure normal to the layer, and sometimes showing a mamillated surface. A few minute needles of wavellite (determined by X-rays) are also present. The minyulite crystals form a thin continuous crust on this apatite, with the crystals closely and confusedly crowded together. It is present in only a few of the cavities and in sparing amount. The crystals are colourless and transparent (water-clear) with a bright vitreous lustre. They are of a short-prismatic habit with a length less than 1 mm. and a width of about one-half or one-third of their length. Although the crystals are so brilliant only approximate

¹ The rock phosphate deposit associated with Cambrian rocks with overlying Tertiary beds at this locality has been described in detail by R. L. Jack, The phosphate deposits of South Australia. Bull. Dept. Mines, South Australia, 1919, no. 7, 136 pp. (pp. 112-115).

² E. S. Simpson and C. R. LeMesurier, Minyulite, a new phosphate mineral from Dandagan, W.A. Journ. Roy. Soc. Western Australia, 1933, vol. 19 (for 1932-33), pp. 13-16. [M.A. 5-293.]

goniometric measurements could be obtained. Images are multiple due to sub-parallel growth, and are further confused by reflection from the back faces. Only three crystal-forms are present: $m(110)$, $c(001)$, and $p(111)$. One series of measurements on three crystals gave the mean values cp $39^\circ 22'$, mm $85^\circ 37'$ (corresponding to $a:b:c = 0.926:1:0.557$); and on another crystal cp $39^\circ 11'$, mm $87^\circ 24'$ ($a:b:c = 0.956:1:0.563$). The second of these approximate axial ratios is nearer to those obtained by Mr. Bannister by X-ray methods (p. 312). There is a perfect cleavage parallel to (001). Etched figures produced by the action of hydrochloric acid on the prism faces (fig. 1) suggest that the crystals are hemimorphic; but on at least one of the measured crystals p faces were found at both ends.

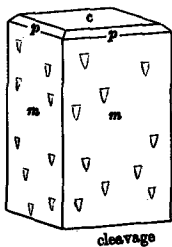


FIG. 1. Crystal of minyulite showing etched figures.

The prismatic crystals show straight optical extinction with negative elongation. The optic axial plane is parallel to (100) and the acute positive bisectrix is normal to (010) with large axial angle. Refractive indices determined by the Duc de Chaulnes method by focusing on etched figures through the prism faces (through a thickness of 0.16 mm.) gave 1.5 and 1.6 as approximate values. Mr. Bannister has recently obtained by the immersion method the values α 1.525, γ 1.530, and has confirmed that $2V$ is large with positive sign. The specific gravity was determined as 2.46 by the pyknometer method on 1.658 g. of separated material.

Material chiselled out of the crystal-lined cavities was separated in diluted methylene iodide from the associated apatite. The lightest fraction consisted of a nearly pure crystalline powder with only a few white and yellowish grains. A portion of this material was used for qualitative chemical tests. The mineral is soluble in warm dilute HCl or HNO₃. Heated in a bulb-tube it readily gives off water which is acid and etches the glass. After this heat-treatment the crystals are white and opaque, but they still retain their form and bright lustre. Before the blowpipe it is difficultly fusible to a blebby glass. One gram of the material was heated at different temperatures with the following results:

Temperature	...	110°	150°	182°	219°	235°	243°	Redness
Loss in weight	...	0.4	0.6	13.7	16.6	17.5	18.2	19.8 %

At redness over the Bunsen burner for $\frac{1}{2}$ hour the material was partly fused on the surface, and after a second $\frac{1}{2}$ hour it was completely fused (sintered) on the surface.

This ignited material remained in the porcelain crucible until 1941, when it was used for the analysis made by Miss Bennett. Heated over a Meker burner there was a further slight loss bringing the total loss up to 20.4 %. As the presence of potassium was not suspected her first analysis showed a low summation; her second analysis is given under I in table I. This as recalculated by Dr. Hey leads to the formula $K_2Al_4(PO_4)_4(OH,F)_2 \cdot 8H_2O$, which also represents the contents of the unit cell determined by X-rays. It differs from Dr. Simpson's formula only in showing one more molecule of water.

The habit of the crystals from Western Australia differs from that of the South Australian occurrence. The former occur as radiating groups of fine fibres

TABLE I. Chemical analysis of minyulite from South Australia.

	I.	IIa.	IIb.	III.		IVa.	IVb.
P ₂ O ₅ ...	43.18	38.00	38.77	38.07	P ...	4.01	4.09
Al ₂ O ₃ ...	34.01	27.79	28.36	27.32	Al ...	4.09	4.17
Fe ₂ O ₃ ...	0.91	0.80	0.82	—	Fe ...	0.08	0.08
MgO ...	0.09	0.08	0.08	—	Mg ...	0.01	0.01
CaO ...	0.86	0.76	0.77	—	Ca ...	0.10	0.10
Na ₂ O ...	0.27	0.24	0.24	—	Na ...	0.06	0.06
K ₂ O ...	12.00	10.35	10.56	12.62	K ...	1.65	1.68
F ...	n.d.	2.7	2.7	2.55	F ...	1.1	1.1
H ₂ O ...	—	20.4	18.8	20.51	OH ...	0.9	0.9
SiO ₂ ...	5.44	—	—	—	O ...	16.2	16.6
					H ₂ O ...	8.0	7.4
	96.76	101.12	101.10	101.07			
Less O for F ₂ —	—	1.1	1.1	1.07			
		100.0	100.0	100.0			

I. Analysis of the ignited material (0.2500 g.), by Miss Hilda Bennett; alkalis by M. H. Hey. The material had lost 20.4% on ignition and still contained some fluorine. A fluorine determination made on 10 mg. of the original un-ignited material gave F 2.7% approximately.

II. Analysis I recalculated (by M. H. Hey) deducting SiO₂ and some Al₂O₃ and K₂O representing fragments of porcelain from the broken crucible in which the material had sintered: (a) on the assumption that no fluorine was lost on ignition; (b) that all the fluorine was lost. Since acid water is expelled on heating, whilst fluorine was shown to be still present in the ignited material, the true composition must be between IIa and IIb.

III. Calculated percentage composition for the formula K₂Al₄(PO₄)₄(OH,F)₂.8H₂O with OH:F = 1:1.

IV a and b. Number of atoms per unit cell calculated from IIa and IIb, sp. gr. 2.46, and the unit-cell dimensions *a* 9.35, *b* 9.74, *c* 5.52 Å.

resembling wavellite in appearance, on the surface of crevices in phosphatic ironstone; but the essential characters are the same for both.

	Western Australia (E. S. Simpson)	South Australia. (F. A. B.)
α ...	1.531	1.525
β ...	1.534	—
γ ...	1.538	1.530
Sp. gr. ...	2.45	2.46 (L. J. S.)

Dr. Simpson stated that the fibres gave straight extinction with negative elongation. His rather higher values for the refractive indices may be related to the lower amount of fluorine present. In the analysis by LeMesurier (table III) fluorine is listed as a 'trace' and the summation is low; but it is stated that when the mineral was dissolved in H₂SO₄ glass was etched, and when it was heated much acid water, also etching glass, was given off, suggesting the presence of more than a 'trace' of fluorine, as further implied by the formula that was given.

The mean refractive index of fluorine-free minyulite, calculated by Dr. Hey from the refractive indices determined by Mr. Bannister (mean $(\alpha + \gamma)/2 = 1.527_6$) and the specific refractive energies ($k = (n-1)d$) H₂O 0.340, O 0.203, F 0.043, listed by Larsen and Berman,¹ is 1.540. Simpson found $(\alpha + \beta + \gamma)/3 = 1.534$, which suggests that his fluorine content is much more than a 'trace'—in fact, it may be round about 1 or 1½%.

¹ E. S. Larsen and H. Berman, The microscopic determination of nonopaque minerals. 2nd edit., Bull. U.S. Geol. Surv., 1934, no. 848, p. 31.

X-ray examination of the crystals from South Australia has recently been undertaken by Mr. Bannister. Laue photographs confirm the orthorhombic symmetry and rotation photographs give the dimensions of the unit cell as a 9.35, b 9.74, c 5.52 Å. ± 0.02 , cell volume 502.7 Å.³, $a:b:c = 0.960:1:0.567$.

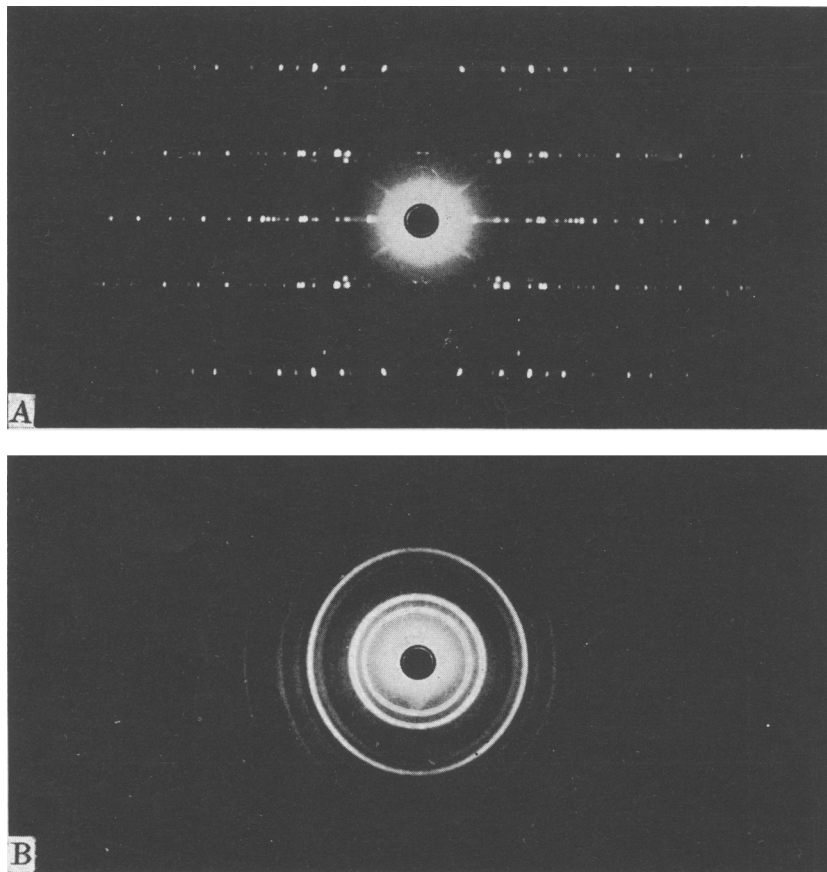


FIG. 2. X-ray photographs of minyulite from Wait's quarry, Noarlunga, South Australia: (A) rotation photograph [001] of a single crystal; (B) powder photograph. Films taken with unfiltered copper radiation, λ 1.539 Å., in a cylindrical camera, 6 cm. diameter. Actual size.

Fig. 2A reproduces the rotation photograph of a crystal of minyulite about the c -axis. Oscillation photographs show that there are no halvings; hence the space-group is $C_{2v}^1 = Pmm$, which permits the following positions for the unit cell contents: 2K in a two-fold position $e, f, g, \text{ or } h$; 4Al in a general position, i ; 4(PO₄) in a general position, i ; 2(OH,F) in a two-fold position $e, f, g, \text{ or } h$; 8H₂O in two sets of general positions, i .¹ None of the atoms is fixed by symmetry con-

¹ Internationale Tabellen zur Bestimmung von Kristallstrukturen. Berlin, 1935, vol. 1, p. 103. [M.A. 6-145.]

ditions and sixteen parameters would need to be calculated from intensity data in order to determine the crystal-structure.

Table II gives the spacings and intensities of powdered minyulite (fig. 2B) which are identical with those obtained for the original minyulite from Western Australia, a paratype of which was presented by Dr. Simpson to the British Museum in 1933 (B.M.1933,84). A rotation photograph of a small splinter of the latter specimen shows that the elongation of the needles making up the stellate aggregates is $c[001]$. It is doubtful whether this specimen would yield a single crystal fibre suitable for the X-ray determination of symmetry and of axial ratios.

TABLE II. X-ray powder photograph of minyulite (fig. 2B). Spacings in Ångström units and estimated intensities. Taken with unfiltered copper radiation, λ 1.539 Å., in a cylindrical camera, 6 cm. diameter.

6.8	m	2.59	m	1.57*	m	1.209	m	0.984	vw
5.6	vs	2.43	}	1.498	vw	1.186	m	0.958	m
4.8*	w	2.25		1.478	m	1.165	w	0.943	vw
4.19*	w	2.12	m	1.432	m	1.131*	vw	0.932	vw
3.72*	m	2.01	w	1.387*	vw	1.110	w	0.919	w
3.37*	vs	1.91	w	1.332*	m	1.069	w	0.901*	w
3.04	w	1.81	w	1.300	w	1.049	vw	0.884	vw
2.94	w	1.74	w	1.278	vw	1.036	vw	0.870	w
2.85	vw	1.69	m	1.259	w	1.021	w	0.861	w
2.69	m	1.61	w	1.237	w	0.999	vw	0.851	w

* Doublets. Bracketed lines are unresolved bands consisting of several lines, and the spacings and intensities of the limits are given.

In conclusion, table III collects together for direct comparison the several published chemical analyses of hydrous K-Al phosphates. If found in quantity these minerals¹ (especially minervite, which contains also ammonium and occurs in recent guano deposits) would be of value as fertilizers for plant growth. X-ray, optical, and density data have been determined by Mr. Bannister for such of these minerals as are available in the British Museum collection. All of them are distinct from minyulite. Details will be given in a later paper.

TABLE III. Chemical analyses of hydrous K-Al phosphates.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
P ₂ O ₅ ...	38.00	35.58	35.05	37.28	35.17	42.70	40.85	37.10	37.89	34.64	33.60
Al ₂ O ₃ ...	27.79	29.98	21.43	18.59	18.18	21.00	20.59	22.89	25.21	27.79	36.03
Fe ₂ O ₃ ...	0.80	trace	4.45	0.83	—	2.90	0.19	1.17	—	—	—
MgO ...	0.08	nil	—	0.33	trace	—	—	trace	trace	nil	0.22
CaO ...	0.76	nil	0.55	1.40	0.31	—	—	trace	12.80	18.10	6.80
Na ₂ O ...	0.24	0.45	trace	—	—	—	—	0.02	1.56	3.08	3.00
K ₂ O ...	10.35	12.30	4.20	8.28	5.80	1.20	8.95	8.04	4.84	2.25	1.64
(NH ₄) ₂ O	—	—	—	0.52	0.48	3.47	trace	0.90	—	—	—
F ...	2.7	trace	—	trace	—	—	nil	—	—	—	—
H ₂ O ...	20.4	20.63	33.06	28.20	28.30	29.80	27.79	29.16	16.80	14.19	17.88
Insol. ...	—	—	0.80	4.35	11.60	—	1.09	0.36	1.10	0.58	—
	101.12	98.94	100.00	99.78	99.84	101.07	99.46	99.64	100.20	100.63	99.17

I. Minyulite, Wait's quarry, Noarlunga, Adelaide Co., South Australia. Miss Hilda Bennett, recalculated by M. H. Hey.

II. Minyulite, Minyulo Well, Dandaragan, Western Australia. E. S. Simpson and C. R. LeMesurier, 1933 (loc. cit.).

¹ They also contain traces of magnesium, which in small amount is an essential constituent of chlorophyll C₅₅H₇₂O₅N₄Mg.

- III. Taranakite, Sugarloaves, Moturoa, New Plymouth, Taranaki, New Zealand. J. Hector and W. Skey, Reports of the Jurors, New Zealand Exhibition, 1865, Dunedin, 1866, p. 423. Also Cl 0.46, SO₃ trace; iron as FeO.
- IV. Minervite, Minerva grotto, Fauzan, dép. Hérault, France. A. Carnot, Ann. des Mines, 1895, ser. 9, vol. 8, p. 319. Also Cl, SO₃ traces.
- V. Minervite, Tour-Combes grotto, Misserghin, Oran, Algeria. A. Carnot, Compt. Rend. Acad. Sci. Paris, 1895, vol. 121, p. 153.
- VI. Minervite, basalt cave, St. Paul, Reunion, Indian Ocean. F. Pisani, analyst. A. Lacroix, Bull. Soc. Franç. Min., 1910, vol. 33, p. 34.
- VII. Minervite, Jenolan Caves, New South Wales. J. C. H. Mingaye, Rep. Australasian Assoc. Adv. Sci., 1898, vol. 7, p. 230; Rec. Geol. Surv. New South Wales, 1899, vol. 6, p. 113. Mean of two closely agreeing analyses.
- VIII. Palmerite, Monte Alburno, Salerno, Italy. E. Casoria, Atti R. Accad. Georgofili, Firenze, 1904, ser. 5, vol. 1, p. 293; Ann. R. Scuola Sup. Agric. Portici, 1904, vol. 6.
- IX. Englishite, Fairfield, Utah. E. S. Larsen and E. V. Shannon, Amer. Min., 1930, vol. 15, p. 328. [M.A. 4-343.]
- X. Lehiite, Fairfield, Utah. Larsen and Shannon, *ibid.*, p. 331.
- XI. Millisite, Fairfield, Utah. Larsen and Shannon, *ibid.*, p. 330.
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