

Biphosphammite: a second occurrence

M. W. PRYCE, B.Sc.

Government Chemical Laboratories, Perth, Western Australia

SUMMARY. Biphosphammite, $\text{NH}_4\text{H}_2\text{PO}_4$, recorded once as secondary powder in 1870, occurs with bat guano in Murra-el-elevyn cave, $31^\circ 20' \text{ S.}$, $126^\circ 0' \text{ E.}$, Western Australia.

The mineral occurs as tapering tetragonal prisms with pyramidal terminations, which are colourless to light buff, very soft, water soluble, contain fine syngenite inclusions, and have D 2.04, ω 1.525, ϵ 1.480. Space group $I\bar{4}2d$, a 7.4935 Å, c 7.340 Å, six strongest powder X-ray lines 3.75 Å (10) 200; 5.24 Å (9) 101; 3.02 Å (9) 112; 1.993 Å (8) 312,213; 2.65 Å (7) 220; 2.368 Å (7) 310,301. Partial analysis of purest available material gave: P_2O_5 51.1, K_2O 14.2, $(\text{NH}_4)_2\text{O}$ 12.3, SO_3 5.59, Na_2O 0.16, water-insolubles 0.81 per cent, remainder mainly CaO and H_2O . Calculated mineral content is 88 % biphosphammite (62 % $\text{NH}_4\text{H}_2\text{PO}_4$, 38% isomorphous KH_2PO_4), 11.5% syngenite, insolubles 0.81 % calc. total 100.3 per cent.

Material proposed to be neotype is preserved at the Government Chemical Laboratories, Perth, Western Australia.

IN 1967 while exploring Murra-el-elevyn cave ($31^\circ 20' \text{ S.}$, $126^\circ 0' \text{ E.}$) on the Nullarbor Plain, Western Australia, P. J. Bridge collected some unusual crystals associated with bat guano. At the W.A. Government Chemical Laboratories, L. V. Bastian identified the crystals as $(\text{NH}_4, \text{K})\text{H}_2\text{PO}_4$, the second record of the mineral biphosphammite and the first *in situ* occurrence.

The first record was by C. U. Shepard, Sr., (1870) who studied a bird guano shipment from Guañape Island ($8^\circ 25' \text{ S.}$, $79^\circ 25' \text{ W.}$) at Charleston, South Carolina, U.S.A.

Shepard noted that lumps and crystal coatings of phosphammite, $(\text{NH}_4)_2\text{HPO}_4$, lost ammonia on exposure to become coated with a powder of secondary biphosphammite, $\text{NH}_4\text{H}_2\text{PO}_4$.

*Occurrence.*¹ Murra-el-elevyn cave is close to the Eyre Highway and approximately 130 miles east of Balladonia. The surface expression of the cave is a fresh collapse doline 60 ft in diameter with sheer 30 ft walls in the flat Nullarbor Plain. Underground the cave slopes steeply for 500 ft to a lake at a vertical depth of 270 ft, then continues horizontally for a further 400 ft as a wide low undulating chamber inhabited by a maternity colony of *Chalinolobus morio* GRAY (the Little Chocolate Bat) identified by Hamilton-Smith (1965).

The biphosphammite occurs as rounded crusts coating the walls and floor, apparently as a crystalline product of the liquid fraction of bat guano.

Physical properties. The biphosphammite is a finely granular crust with raised radiating groups of crystals, mainly tapering prisms as large as 2 mm long and 0.2 mm

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¹ Described by P. J. Bridge, Government Chemical Laboratories, Perth, W.A.

thick. Syngenite is closely intergrown and also enclosed in the biphosphammite crystals.

The crust has a dull earthy appearance and varies from white through to deep shades of brown. The crystals are very soft with a dull lustre and occasional vitreous clusters. The streak is between white and Ridgway (1912) Light Buff 17f. Using the sink-float method in diluted bromoform some of the cleanest crystals gave $D 2.04 \pm 0.02$, which would be a little high due to inclusions of syngenite.

Optical properties. The crystals are colourless with many fine syngenite inclusions and have $\omega 1.525$, $\epsilon 1.480$. By the same method Analar grade $\text{NH}_4\text{H}_2\text{PO}_4$ and KH_2PO_4 gave $\omega 1.525$, $\epsilon 1.480$ and $\omega 1.510$, $\epsilon 1.468$ respectively, in good agreement with Winchell and Winchell (1964).

Chemistry. A sample was prepared for analysis from the small amount of relatively pure crystals by centrifuging with diluted bromoform. The final concentrate still contained fine inseparable syngenite inclusions.

A partial analysis by P. Hewson using standard methods gave P_2O_5 51.1, K_2O 14.2, $(\text{NH}_4)_2\text{O}$ 12.3, SO_3 5.59, Na_2O 0.16, water-insoluble fraction 0.81 %, remainder mainly CaO and H_2O . Calculation to constituent minerals gave 88.0 % biphosphammite of composition 62 % ammonium salt $\text{NH}_4\text{H}_2\text{PO}_4$ with 38 % isomorphous potassium salt KH_2PO_4 . The remainder consisted of 11.5 % syngenite, insolubles 0.81 %, calculated total 100.3 %.

X-ray data. Weissenberg photographs confirmed that the biphosphammite conforms to space group $I\bar{4}2d$. Some disorder along c in the crystals is indicated by the 008 and 208 reflections being recorded on the films as unresolved streaks.

A unit-cell refinement gave the values $a 7.4935 \pm 0.0005 \text{ \AA}$, $c 7.340 \pm 0.003 \text{ \AA}$, $c/a 0.9795$, $V 412.2 \text{ \AA}^3$ for biphosphammite. The length of c corresponds to a composition 64 % $\text{NH}_4\text{H}_2\text{PO}_4$ and 36 % KH_2PO_4 .

The powder X-ray data, Table I, were measured on films taken with a Guinier-Hagg focusing camera with $\text{Cu-K}_{\alpha 1}$ radiation and ThO_2 internal standard. Coates and Woodard (1963) produced powder data with similar d spacings from artificial (0.73 $\text{NH}_4\text{H}_2\text{PO}_4$)·(0.27 KH_2PO_4) formed in fertilizer.

Unit cell refinements of Analar grade chemicals gave $a 7.4987 \pm 0.0005 \text{ \AA}$, $c 7.550 \pm 0.005 \text{ \AA}$ for $\text{NH}_4\text{H}_2\text{PO}_4$ and $a 7.451 \pm 0.001 \text{ \AA}$, $c 6.972 \pm 0.0015 \text{ \AA}$ for KH_2PO_4 , in good agreement with the results of Swanson and Fuyat (1953) and Swanson, Fuyat, and Ugrinic (1953). The refinements were all done by the method described by Pryce (1970). All X-ray exposures were made in the range 15 to 20 °C.

Conclusions. The density and c -axis measurements of biphosphammite correspond closely to the chemical composition on analysis but the refractive indices are close to those of pure $\text{NH}_4\text{H}_2\text{PO}_4$. There is no obvious reason, although minerals are occasionally found to have different refractive indices from the more-pure artificial equivalents.

Neotype material is preserved at the Government Chemical Laboratories, Perth, Western Australia.

TABLE I. *X-ray powder diffraction data for biphosphammite (NH₄:K = 61:39). Guinier focusing camera, Cu-K_{α1}, ThO₂ internal standard.*

<i>hkl</i>	<i>I</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>hkl</i>	<i>I</i>	<i>d</i> _{obs}	<i>d</i> _{calc}
101	9	5.24 Å	5.244 Å	431	4	1.470 Å	{1.468 Å
200	10	3.75	3.747	413}			{1.459
211	4	3.05	3.048	521	2	1.365	{1.367
112	9b	3.02	3.017	512}			{1.364
220	7	2.650	2.649	440	3	1.324	1.325
202	4	2.623	2.622	404	3b	1.310	1.311
310}	7	2.368	{2.369	530}	2	1.285	{1.285
301}			{2.365	503}			{1.278
321	5	2.002	2.000	433}	1	1.270	{1.278
312}	8	1.993	{1.991	334}			{1.273
213}			{1.976	442	3b	1.250	1.246
400	1	1.875	1.873	424	3b	1.240	1.237
303	3b	1.754	1.748	532}	3b	1.214	{1.213
420}	4	1.676	{1.675	523}			{1.210
402}			{1.669	620	4	1.186	1.185
332	6	1.593	1.591	602	2	1.182	1.182
323	3b	1.586	1.584	541	1	1.156	1.156
422	3b	1.515	1.524	514	1	1.150	1.147
224	3b	1.510	1.509	631	4	1.105	1.104
				613	2	1.100	1.100

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