MINERALOGICAL MAGAZINE, DECEMBER 1972, VOL. 38, pp. 965–7.

Biphosphammite: a second occurrence

M. W. PRYCE, B.Sc.

Government Chemical Laboratories, Perth, Western Australia

SUMMARY. Biphosphammite, $NH_4H_2PO_4$, recorded once as secondary powder in 1870, occurs with bat guano in Murra-el-elevyn cave, 31° 20′ S., 126° 0′ 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, $(NH_4)_2O$ 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 % $NH_4H_2PO_4$, 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° 20′ S., 126° 0′ 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 $(NH_4, K)H_2PO_4$, 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° 25′ S., 79° 25′ W.) at Charleston, South Carolina, U.S.A.

Shepard noted that lumps and crystal coatings of phosphammite, $(NH_4)_2HPO_4$, lost ammonia on exposure to become coated with a powder of secondary biphosphammite, $NH_4H_2PO_4$.

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

---

[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 17′f. Using the sink–float method in diluted bromoform some of the cleanest crystals gave D 2·04±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 ω 1·525, ϵ 1·480. By the same method Analar grade $NH_4H_2PO_4$ and KH_2PO_4 gave ω 1·525, ϵ 1·480 and ω 1·510, ϵ 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, $(NH_4)_2O$ 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 $NH_4H_2PO_4$ 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±0·0005 Å, *c* 7·340±0·003 Å, *c*/*a* 0·9795, *V* 412·2 Å^3 for biphosphammite. The length of *c* corresponds to a composition 64 % $NH_4H_2PO_4$ and 36 % KH_2PO_4.

The powder X-ray data, Table I, were measured on films taken with a Guinier–Hagg focusing camera with 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 $NH_4H_2PO_4$).(0·27 KH_2PO_4) formed in fertilizer.

Unit cell refinements of Analar grade chemicals gave *a* 7·4987±0·0005 Å, *c* 7·550±0·005 Å for $NH_4H_2PO_4$ and *a* 7·451±0·001 Å *c* 6·972±0·0015 Å 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 $NH_4H_2PO_4$. 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* (NH_4:K = 61:39). *Guinier focusing camera,* Cu-$K_{\alpha 1}$, ThO_2 *internal standard.*

hkl	*I*	d_{obs}	d_{calc}	*hkl*	*I*	d_{obs}	d_{calc}
101	9	5·24 Å	5·244 Å	431 413	4	1·470 Å	1·468 Å 1·459
200	10	3·75	3·747	521 512	2	1·365	1·367 1·364
211	4	3·05	3·048	440	3	1·324	1·325
112	9b	3·02	3·017	404	3b	1·310	1·311
220	7	2·650	2·649	530 503	2	1·285	1·285 1·278
202	4	2·623	2·622	433 334	1	1·270	1·278 1·273
310 301	7	2·368	2·369 2·365	442	3b	1·250	1·246
321	5	2·002	2·000	424	3b	1·240	1·237
312 213	8	1·993	1·991 1·976	532 523	3b	1·214	1·213 1·210
400	1	1·875	1·873	620	4	1·186	1·185
303	3b	1·754	1·748	602	2	1·182	1·182
420 402	4	1·676	1·675 1·669	541	1	1·156	1·156
332	6	1·593	1·591	514	1	1·150	1·147
323	3b	1·586	1·584	631	4	1·105	1·104
422	3b	1·515	1·524	613	2	1·100	1·100
224	3b	1·510	1·509				

Acknowledgements. The author is grateful to E. Maslen, B. H. O'Connor, and A. O'Connell, for advice and assistance.

The work was done and published with the permission of the Director of the W.A. Government Chemical Laboratories.

REFERENCES

COATES (R. V.) and WOODARD (G. D.), 1963. *Journ. Sci. Food Agric.* **14,** 398.

HAMILTON-SMITH (E.), 1965. *Western Caver,* **5** (3), 1.

HENDRICKS (S. B.), 1927. *Amer. Journ. Sci.* **14,** 269.

HUTCHINSON (G. E.), 1950. Survey of contemporary knowledge of biogeochemistry, 3. The biogeochemistry of vertebrate excretion. *Bull. Amer. Mus. Nat. Hist.* **96** [M.A. **11**-245].

PRYCE (M. W.), 1970, *Journ. Phys. E*: **3,** 1026. [M.A. **23**-72]

RIDGWAY (R.), 1912. *Color Standards and Color Nomenclature.* Baltimore (A. Hoen & Co.).

SHEPARD (C. U., *Sr.*), 1870. *Rural Carolinian,* **1,** 467.

SWANSON and FUYAT, 1953. *Nat. Bur. Standards Circular* no. 539 III, 69, June 10, 1954.

SWANSON, FUYAT, and UGRINIC, 1953. Ibid. no. 539 IV, 64, 1955.

UEDA (R.), 1948. *Journ. Phys. Soc. Japan,* **3,** 328 [M.A. **11**-240].

WEST (J.), 1930. *Zeits. Krist.* (A) **74,** 306 [M.A. 4-366].

WINCHELL (A. N.) and WINCHELL (H.), 1964. *The Microscopical Characters of Artificial Inorganic Solid Substances,* 3rd edn, 138, 187. New York–London (Academic Press Inc.) [M.A. **17**-15].

[*Manuscript received 14 January 1972*]