

Urea, a new mineral, and neotype phosphammite from Western Australia

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SUMMARY. Urea, a new mineral identical with the artificial compound, occurs as crystals associated with phosphammite, ammonian aphthitalite, and weddellite in guano from Toppin Hill, 123° 56' E., 28° 42' S., Western Australia. The urea occurs as elongated tetragonal pyramids, space group $P4_21m$, a 5.646, c 4.701 Å, X-ray powder data are given. Optical properties: ω 1.484, ϵ 1.603. Chemical analysis gave urea, $\text{CO}(\text{NH}_2)_2$ 96.0, H_2O^- 0.46, Na 0.13, K 0.35, Ca 0.07, Mg 0.03, S 0.11, P 0.24, NH_3 < 1.0 %, remainder probably mainly H_2O^+ ; urea 96 %, impurities 4 %. Type material is preserved in the collection of the Government Chemical Laboratories, Perth, Western Australia.

DURING an investigation of cave minerals at the Western Australian Government Chemical Laboratories specimens from the collection of Dr. E. S. Simpson acquired early this century were re-examined. An unusual specimen marked 'Struvite or stercorite efflorescence on guano' was found to consist of urea crystals with minor ammonian aphthitalite, weddellite, and phosphammite.

The specimen was donated by Frank Hann, a pastoralist and explorer for the Department of Lands and Surveys who named Toppin Hill in 1906. The locality given 'Earles' or 'Earls Find' a name that cannot be traced in any government records. A later label note by Dr. Simpson is 'Mt. Toppin near Lake Rason'. The present accepted name is Toppin Hill, 123° 56' E., 28° 42' S., about 200 miles NE. of Kalgoorlie. The occurrence was probably in a cave or rock shelter. The highly soluble material persists because of the low humidity and rainfall, 8 in., and the high average annual temperature range, 12 °C to 26 °C.

Urea, discovered in urine in 1773, was the first of the organic compounds to be synthesized, in an epoch-making discovery by Friedrich Wöhler in 1828. 'I can make urea without the necessity of a kidney, or even an animal, whether man or dog. Ammonium cyanate is urea.' Liebig considered this the first beginning of a truly scientific organic chemistry (Partington, 1964).

Urea, the main nitrogenous component of the urine of animals with ureotelic metabolisms, rarely occurs in guano because of its solubility and instability in humid and bacterial conditions, under which decomposition is very rapid. Popp (in Hutchinson, 1950) described a crystalline, stalactitic accumulation mainly composed of urea derived from the rapid evaporation of bat urine on the wall of a very dry Egyptian cave, conditions which inhibit decomposition. Hey (1972, pers. comm.) reports urea as a rather recent efflorescence on sand from the Temple of Dendera in the Egyptian desert.

To avoid duplexity of names the author does not propose to exercise his prerogative to assign another name to the well-known chemical compound.

Physical properties. The specimen consists of a damp incoherent mass of pyramidal urea crystals, 3×1 mm, translucent and a pale yellow to pale brown. The ammonian apthitalite, which may be shrivelled bat droppings, occurs as dark brown soft finely-crystalline aggregates 1 mm in diameter. The phosphammite exists as sparse transparent crystals 0.5 mm in size grown on the ammonian apthitalite. The weddellite is present in small amounts as pale yellow crystal aggregates. Using the sink-float method in Nujol and α -bromonaphthalene some clean urea crystals gave $D_{1.33} \pm 0.01$. The remaining physical properties are the same as for the artificial material.

TABLE I. X-ray powder data for urea. Guinier focusing camera, Cu-K α_1 radiation, KCl internal standard, I visual

<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}
001	< 1	4.70 Å	4.701 Å	221	1	1.837 Å	1.837 Å
110	10	3.98	3.992	310	< 1	1.785	1.785
101	2	3.61	3.613	301	< 1	1.746	1.747
111	3	3.04	3.043	212	< 1	1.721	1.720
200	< 1	2.822	2.823	311	< 1B	1.669	1.669
210	1B	2.522	2.525	003	< 1	1.567	1.567
201	< 1B	2.419	2.420	222	< 1	1.522	1.522
002	< 1	2.352	2.350	103	< 1	1.509	1.510
211	< 1	2.224	2.224	312	< 1	1.422	1.422
102	1	2.172	2.170	330	< 1B	1.331	1.331
112	< 1	2.026	2.026	420	< 1	1.263	1.262
220	< 1	1.996	1.996	004	< 1	1.177	1.175
				114	< 1	1.129	1.127

X-ray data. The powder X-ray data of the natural urea (Table I) was measured on films taken with a Guinier-Hagg focusing camera using Cu-K α_1 radiation and KCl internal standard. The data of natural and Analar grade urea showed only slight differences from the published data except that the 001 reflection at 4.7 Å, not recorded from the published pattern, was observed on patterns of both natural and artificial samples. In addition, some of the published faint lines were not observed while some extra faint lines were seen.

Weissenberg photographs confirmed that the urea conforms to space group $P\bar{4}2_1m$. A unit cell refinement gave a 5.646 Å, c 4.701 Å, both ± 0.001 Å, $c/a = 0.8326$, $V = 149.86$ Å³ for the mineral urea, similar to artificial urea. Unit cell refinement of Analar grade urea gave a 5.648 Å, c 4.701 Å, both ± 0.001 Å, $c/a = 0.8323$, V 149.96 Å³ in close agreement with the work of the National Bureau of Standards (1957). The refinements were done by the method described by Pryce (1970). All X-ray exposures were made in the range 15–20 °C.

Chemistry. Analysis by B. Codling and P. Hewson of hand-picked crystals gave 96% urea by the urease reduction method, plus NH₃ < 1.0, Na 0.13, Ca 0.07, K 0.35, Mg 0.03, S 0.11, P 0.24, H₂O⁻ 0.46, remainder probably mainly H₂O⁺.

Optical Properties. The crystals of mineral urea have ω 1.484 and ϵ 1.603 and are similar to the reported ω 1.480 and ϵ 1.601, National Bureau of Standards (1957) and ω 1.484 ϵ 1.602 (Winchell, 1954).

PHOSPHAMMITE and biphosphammite were described by Shepard (1870) from the Guañape Islands, 8° 25' S., 79° 25' W., and both have long been considered doubtful species (Dana, 1892). Pryce (1972) has described biphosphammite discovered by the present author, from Murra-el-elevyn Cave in the Nullarbor Plain, 240 miles SE. of this occurrence. The phosphammite shows close correlation with ASTM data card 9-391, 'secondary ammonium orthophosphate' $(\text{NH}_4)_2\text{HPO}_4$. Refractive indices are close to the artificial compound.

The natural occurrence of $(\text{NH}_4)_2\text{HPO}_4$ is thus confirmed and the specimen is proposed as a neotype.

The ammonian apthitalite and weddellite powder patterns showed no significant difference from the published patterns. All patterns gave a few faint extra lines of minor unidentified components.

Acknowledgements. This work was carried out and published with the permission of the Director of the Western Australian Government Chemical Laboratories. The author expresses his appreciation of the help given by colleagues.

REFERENCES

- DANA (E. S.), 1892. *System of Mineralogy*, 6th edn, New York (John Wiley & Sons, Inc.).
 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].
 National Bureau of Standards (1957). *Circular 539, Standard X-ray diffraction powder patterns*, 7, 61-2.
 PARTINGTON (J. R.), 1964. *A History of Chemistry*, 4, 259-60. London (Macmillan & Co. Ltd.).
 PRYCE (M. W.), 1970. *Journ. Phys. E.*, **3**, 1026 [M.A. 72-773].
 — 1972. *Min. Mag.* **38**, 965-7 [M.A. 73-797].
 SHEPARD (C. U., Sr.), 1870. *Rural Carolinian*, **1**, 467.
 WINCHELL (A. N.), 1954. *The Optical Properties of Organic Compounds* 2nd edn, 38. New York (Academic Press Inc.).

[Manuscript received 27 November 1972]