# Guano minerals from Murra-el-elevyn Cave Western Australia

## P. J. BRIDGE

Government Chemical Laboratories, Perth, Western Australia

SUMMARY. Biphosphammite, ammonian  $KH_2PO_4$ , syngenite, aphthitalite, monetite, hannayite, whitlockite, apatite and minor gypsum, taylorite, brushite, mirabilite, guanine, and unidentified compounds form crystalline crusts on the walls and floors of a chamber of Murra-el-elevyn Cave, Cocklebiddy, Nullarbor Plain, Western Australia. The minerals are derived from the interaction of bat urine, droppings, and limestone. Analyses for CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O<sup>-</sup>, total N, and ignition loss are given. High K<sub>2</sub>O and low total N figures are characteristic of the analyses.

MURRA-EL-ELEVYN Cave and the occurrence therein of biphosphammite and syngenite have been described by Dunkley and Wigley (1967) and Pryce (1972). Colonies of *Chalinolobus morio*, Gray (The Little Chocolate Bat), have formed a large guano pile and coated much of the porous limestone rubble floors and boulder piles of the bat chambers with a buff to dark brown-black, massive to crystalline crust scattered with insect remains, bat droppings, dead bats, and skeletal material.

The crusts on the more level surfaces tend to be dull in appearance with few watersoluble minerals, no observable crystals and an abundance of organic coating material. The slopes, ledges, and boulder piles are coated with crystalline crusts, many of which have contracted and exfoliated from the base rock either by drying or by removal of some constituents by solution. The more soluble crystallized minerals occur either on the top of the crusts or on the base where they have lifted away from the limestone. Where these crusts are in direct contact with the limestone no crystals have developed. The massive portion of these crusts consists of intergrown aphthitalite, syngenite, monetite, whitlockite, gypsum, and organic materials in varying amounts.

The crystalline coatings are mainly biphosphammite and ammonian  $KH_2PO_4$ , occurring in buff to white  $2 \cdot 0 \times 0 \cdot 2$  mm tapering prisms. Occasional clear, pale brown, platy,  $0 \cdot 2 - 0 \cdot 5$  mm hannayite crystals are found in groups coating crusts. Brushite and taylorite occur occasionally as scattered or grouped feathery white  $0 \cdot 25 \times 0 \cdot 2$  mm crystals. The guanine is white, fine grained, soft, and covers areas of the crust up to 2 mm diameter. Several other unidentified compounds of possible organic origin were observed. Mirabilite occurs as small clear crystal groups among organic fibres on steep slopes near the guano piles and not usually associated with the crusts. Dahllite occurs as dark brown, smoothly crenulated coatings on higher ledges where the bats probably once roosted.

The ammonian  $KH_2PO_4$  is identical in appearance with the biphosphammite. A full description is in preparation. The taylorite, a potassium ammonium sulphate © Crown copyright reserved.

### P. J. BRIDGE ON

intermediate between arcanite and mascagnite, has optical properties and X-ray powder data that compare well with that of Winchell and Benoit (1951). Guanine was first described by Unger and Einbrodt in 1846 in guano from North Chincha Island, Peru, and Africa (Hutchinson, 1950). The original description and this subsequent identification establish the existence of guanine as an organic mineral of biogeochemical origin. Insufficient material is available for a full description.

Sample	Ι	2	3	4	5	6
CaO	28.5	18.2	14.3	35.7	18.5	16.7
MgO	0.80	1.33	0.60	0.38	0.55	1.59
Na <sub>2</sub> O	6.31	3.36	2.29	0.82	0.77	0.67
K₂O	8.94	15.9	18.0	0.21	13.7	15.3
$(NH_4)_2O$	0.01	0.14	0.36	0.01	0.42	0.35
$P_2O_5$	22.3	23.8	21.9	13.0	28.6	27.1
SO3	18.2	22.8	27.4	25.7	20.3	20.9
$CO_2$	3.31	0.63	0.06	2.48	0.14	0.12
$H_2O^-$	3.09	3.05	2.20	12.6	1.27	1.69
Total N	2.20	1.54	1.41	0.43	2.17	0.51
HCl insoluble	0.22	0.52	0.22	0.42	0.30	0.16
Ignition loss						
at 1000 °C	10.0	20.2	30.2	22.0	30.8	30.6
Aphthitalite	х	х	х			х
Biphosphammite	_		X		Х	
Brushite		Х	Х		$\mathbf{X}$ ?	
Calcite	Х	X	_	Х		_
Dahllite				Х		
Guanine			Х		_	X
Gypsum	Х	Х	Х	Х	Х	
Hannayite						X
Ammonian KH <sub>2</sub> PO <sub>4</sub>		_	Х	_	х	Х
Mirabilite	Х					_
Monetite		X	X	Х	Х	X
Syngenite	Х	Х	Х	Х	Х	X
Taylorite		_	Х	_	Х	
Whitlockite	Х	Х	—	X	X	—
Unidentified			Х		X	X

 TABLE I. Murra-el-elevyn crust analyses and mineral distribution. Analyst:

 F. R. W. Lindsey

X present.

The bat colonies are in higher sections of the chambers or in enclosed areas where atmospheric and temperature changes are minimal. The relative humidity was 88 % and the temperature  $18\cdot3$  °C in the main bat chamber. A concentrated solution composed of urine, soluble constituents of the droppings, and minor water from surface drainage has coated the limestone over which it passes forming the crusts. An organic origin of part of the calcium is quite probable as there is a definite demarcation between the crust and limestone and there does not appear to be any further alteration of the limestone.

468

### **GUANO MINERALS**

Breakdown of the bat urine is relatively quick in the humid and bacterial cave conditions. The resulting nitrogenous products have combined with the phosphate, potassium, and calcium to form the suite of unusual minerals.

Chemistry. The analysed crusts vary considerably in colour, appearance, and mineralogy (Table I) but the analyses show only a slight overall variation. Few of the analyses of bat guano in Hutchinson (1950) show  $K_2O$  levels comparable to those reported here except where the materials are taranakite, nitre, or guano ash. With the existence of ammonia-rich minerals higher nitrogen contents would be expected. The low total N and nitrogen to phosphorus ratio indicate almost complete denitrification of the crusts, the remaining N being present in the biphosphammite, ammonian  $KH_2PO_4$ , taylorite, hannayite, insect remains, and other organics. The 10 to 20 % of organic matter has not yet been examined fully and will be the subject of a later note. No analysis of fresh guano or urine from the cave is available.

Combined water could not be determined by conventional methods due to volatilization and decomposition of the sample. No combined water was liberated by the Dean and Stark method using toluene as a solvent at its boiling point of 110 °C. On heating a strong odour was noticed and samples 1 and 4 sintered and the others fused to a white button.

Crusts of similar appearance to the Murra-el-elevyn material have been collected by the author, M. Archer, B. Muir, and R. Shoosmith from other Nullarbor caves: Pannikin Plains, Dingo Donga, Abrakurrie, Weebubbie, and an unnamed cave near Madura. All appear to be leached with the exception of the last which contains biphosphammite.

Specimens are preserved in the collections of the Government Chemical Laboratories, Perth, Western Australia.

Acknowledgements. This work was carried out and published with the permission of the Director, W.A. Government Chemical Laboratories. The author expresses his appreciation of the help of colleagues and members of the W.A. Speleological Group.

#### REFERENCES

DUNKLEY (J. R.) and WIGLEY (T. M. L.), 1967. Caves of the Nullarbor, Sydney. The Speleological Research Council Ltd.

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.), 1972. Biphosphammite: a second occurrence. Min. Mag. 38, 965 [M.A. 73-797.]

WINCHELL (H.), and BENOIT (R. J.), 1951. Taylorite, Mascagnite, Aphthitalite, Lecontite and Oxammite from Guano. Amer. Min. 36, 590-602. [M.A. 11-552.]

[Manuscript received 12 March 1973]