BRUSHITE AND TARANAKITE FROM PIG HOLE CAVE, GILES COUNTY, VIRGINIA

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ABSTRACT

Brushite occurs as nodular masses of platy crystals in the lower part of a bat guano and hair deposit in Pig Hole Cave, Giles County, Virginia. Taranakite occurs as flour-like masses near contacts between the guano and hair deposit and clay and along fractures within brecciated clay within the same cave. Chemical, physical, optical, x-ray, and thermal data for each of these minerals are presented. Some of the thermal data for brushite and many of the data for taranakite are reported here for the first time. It is suggested that the taranakite formed as the result of reactions between the bat guano and bat hair and clay.

INTRODUCTION

The presence of the minerals later identified as brushite and taranakite in a bat guano and hair deposit in Pig Hole Cave, Giles County, Virginia, was discovered in January, 1954. So far as has been ascertained by a search of the literature, this is the first reported natural occurrence of either brushite or taranakite in the United States of America. After positive identification of the minerals, further investigations of them were undertaken mainly because of their relative abundance within the cave.

LOCALITY AND OCCURRENCES

Pig Hole Cave is located beneath the property of A. B. Porterfield on Johns Creek Mountain in southeastern Giles County, southwestern Virginia. The cave was so named because of the former presence within it of the odoriferous remains of a pig lodged in a crawlway beneath the natural opening to the cave.

Pig Hole Cave has received special attention because of its proximity to Blacksburg, the home base of the VPI Cave Club, and because of the presence within the cave of relatively large deposits of bat guano. One natural entrance and one man-made entrance afford access. Entry through the natural entrance is gained by a drop of over 100 feet to the bottom of a sink hole; entry through the man-made entrance is gained by an eight-foot drop through a square tile to a crawlway that enters a room a short distance from the opening. The temperature of the air within the cave has been found to range between 8° C. and 10° C.

The cave is inhabited at the present time by a few "little brown bats" (*Myotis lucifugus lucifugus*) and possibly, as is suggested by fecal re-

mains, by a few other small mammals or possibly owls. Part of a jaw bone identified by H. S. Mosby of the VPI biology department to have belonged to an otter (Lutra) was found in the cave by W. D. Durham, Jr., in 1955. The bone may have been transported into the cave by some predatory animal; in any case, Professor Mosby notes that otters have been "extremely rare if present within the region for the last 50 or more years."

The cave is in a cherty limestone of mid-Ordovician age (B. N. Cooper, personal communication). Numerous fallen blocks (up to 15 feet in largest dimension), paucity of cave deposits, and numerous large rooms and deep wells characterize the cave. A few quartz crystals with curved faces occur attached to the roofs and walls of some passageways in the cave. Notable alluvial deposits constituted of cobbles and boulders of sandstone and quartzite plus silt and clay also occur within the cave. Clusters of transparent gypsum (selenite) crystals occur in the clay of the deposits in a few places; apparently they grew in place. Locally, the alluvial deposits are brecciated, probably as the result of desiccation. Taranakite occurs sporadically between some adjacent fragments of these "breccias."

A pit approximately five feet long, three feet wide, and five and a half feet deep is located about 75 feet from the man-made entrance to the cave. It was dug to investigate the size of the guano deposit in one of the rooms. It was in this pit that the brushite and taranakite were found first. The deposit, as exposed in the pit, has the following section: the upper foot is composed of a felt of brown hair (of bats) interlayered with nearly white excreta (now mostly gypsum); this admixture grades into a laminated white to buff colored zone, also composed of gypsum; the material of the bottom foot is distinctly different from that above— it is brown, generally massive, and contains masses of black carbonaceous material, brushite, and taranakite. The brushite occurs as nodular masses of minute crystals sporadically throughout this lower zone and the taranakite occurs as masses of a flour-like powder restricted to an even narrower zone adjacent to the clay bottom. The taranakite decreases in abundance upward away from the clay. The clay that forms the bottom of the pit is not unlike that of some of the alluvial deposits in the cave. A three to six inches thick zone of black carbonaceous material with small amounts of included gypsum is present between the guano and the limestone of the cave walls.

Previous Work

Brushite and taranakite are both treated in the recent edition of Dana's System of Mineralogy (8). A few short papers dealing at least in

part with the minerals have appeared in the literature since this publication. Some of these papers are referred to directly below. Therefore, it is considered superfluous to include a summary of the literature here.

DESCRIPTIONS

Brushite.—The following properties were determined for the brushite from Pig Hole Cave.

Crystal System: Monoclinic
Physical Properties:
    Thin plates. Perfect micaceous cleavage.
    H.—$2\frac{1}{2}$. G. 2.30. Luster—vitreous.
    Color—ivory yellow (Ridgeway color standard).
    Transparent to translucent.
Optical Properties:
    Colorless in transmitted light
    Indices of Refraction —$\alpha = 1.54$
                        $\beta = 1.544$ (Calc.
    from values of α, γ, and 2V by Mertie method)
                      $\gamma = 1.552$
    Biaxial (+)
    2V = 59 to 65°
    $r < v$, inclined dispersion
    Parallel extinction on laths and upturned edges of plates.
Chemical analysis:

	Formula $CaHPO_4 \cdot 2H_2O$		Theoretical Composition
CaO		31.9	32.6
P_2O_5		40.5	41.2
H_2O		27.5	26.2
		99.9	100.0

Analyst: John Murray
Spectrographic analyses showed presence
    also of Fe, Mg, Al, and Ni.
Solubility—0.0245 gm. of $CaHPO_4 \cdot 2H_2O$/100 gm. water at 25° C.

Thermal data[1]: The heating curve for brushite is presented (Fig. 1). The information derived from x-ray examination of the products that exist after each reaction are noted below. These data corroborate the dehydration work of Sekanina (10) who showed that more than 20 per cent of H_2O is removed below 185° C. and that the remaining approximately 6.5 per cent H_2O is removed between 185° C. and 600° C.

Brushite exists until water is removed (indicated by the first endothermic reaction). Monetite, $CaHPO_4$, then exists until the second reaction. The second endothermic peak apparently manifests the loss of hydrogen (as H_2O), in which case the final product is $Ca_2P_2O_7$. Neither

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[1] Differential thermal equipment used—*FH305* furnace in vertical position heated at the rate of 12.5° C./min.; Leeds and Northrop x-y recorder; Pt+P+10 Rh thermocouple; three point system; scale multiplication of 10.

X-ray data:

X-ray setup—General Electric *XRD*-3 diffraction unit with a No. 1 *SPG* geiger counter type spectrogoniometer; Cu Kα radiation with Ni filter. Also, *d* values and relative intensities were corroborated with Co Kα radiation with an Fe filter.

d, Å	*I*, approx. counts	*d*, Å	*I*, approx. counts
7.62	12,000	1.71	15
4.27	290	1.63	40
3.80	3,700	1.62	50
3.06	900	1.61	50
2.93	80	1.59	30
2.86	20	1.55	15
2.80	15	1.53	35
2.67	70	1.52	50
2.63	160	1.46	70
2.53	770	1.37	50
2.47	55	1.34	40
2.27	100	1.33	45
2.17	115	1.27	160
2.15	50	1.26	100
2.10	30	1.23	50
2.09	20	1.20	15
2.03	30	1.19	15
2.01	180	1.18	15
1.98	20	1.15	30
1.94	20	1.13	35
1.90	1,250	1.09	150
1.86	90	1.08	100
1.82	60	1.06	15
1.80	40	1.057	20
1.78	55	1.05	15

(94 degrees 2θ end of scan)

of these reactions showed reversibility in cooling curves. *X*-ray data for product B_3 are given below because they do not agree with data given for any previously reported calcium pyrophosphate.

PRODUCT B_3

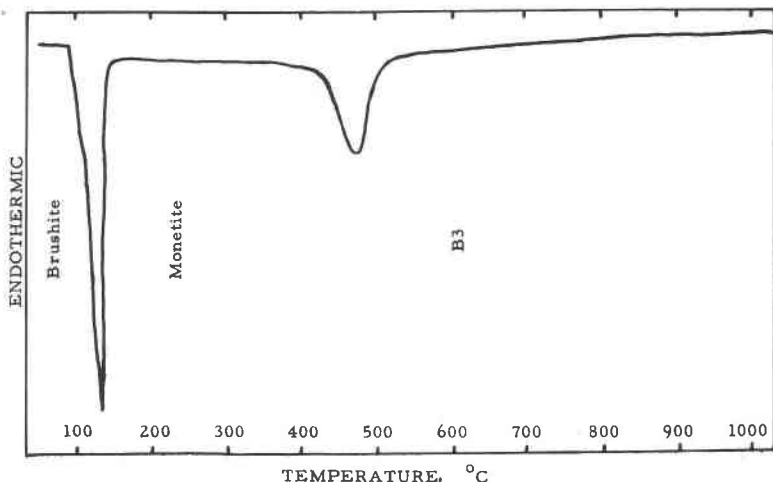| *d*, Å	*I*, approx. counts
3.35	25
3.07	55
2.93 (d)*	50
2.71	10
2.41	10
2.23	20
2.22	15
2.10	10

* "(d)" signifies doublet.

FIG. 1. Tracing of thermal (D.T.A.) curve of brushite.

Taranakite.—Except where noted otherwise, the following properties were determined for the taranakite from Pig Hole Cave.

Crystal system: Hexagonal (?)—on basis of optical uniaxiality and hexagonal shapes shown in photo-electronmicrographs by Haseman, *et al.* and Kittrick and Jackson (7). This does not agree with the "monoclinic . . . pseudo-hexagonal" reported by Haseman, *et al.* (5). However, Lehr (personal communication, 1955) states that " . . . we have extended the study on taranakite well beyond that reported in the paper of Haseman, Lehr, and Smith . . . a single-crystal Weissenberg study revealed that the unit cell is rhombohedral . . . we originally indexed taranakite as a monoclinic cell which is now shown to be a sub-unit of the rhombohedral cell. We did not recognize the rhombohedral character because of the unusually long c-dimension and because the earlier crystal preparations were too small to give good interference figures . . . "; this agrees with the "hexagonal" suggested here.

Physical Properties:
    Massive, flour-like powder.
    Color—white.
    H.—soft G. 2.12. Insoluble.

Optical Properties:
    Colorless in transmitted light
    Indices of refraction: $\omega = 1.506$–1.510
                             $\epsilon = 1.500$–1.503
    Birefringence: 0.006–0.007
    Uniaxial ($-$)
    Parallel extinction of laths.
    (The values given for the indices of refraction are for the taranakite from the breccia and the taranakite from the pit, respectively. Perhaps it is significant that the latter, which has the higher indices, has the higher $(NH_4)_2O$, Fe_2O_3 and H_2O contents.)

Chemical Analysis: The formula corresponding to the analysis of the taranakite from the brecciated clay is $3(K, Na, NH_4, Ca/2)_2O \cdot 5(Al, Fe)_2O_3 \cdot 7P_2O_5 \cdot 43H_2O$. It is apparent

that the bases present are insufficient to form normal phosphates. This is in agreement with the findings of Gautier (3). The formula given in the recent edition of Dana's System of Mineralogy (8) shows a basic phosphate although no analyses reported as yet show a high enough proportion of bases to support such a formula. Haseman *et al.* (5) state that they believe that the composition for taranakite is $2K_2O \cdot 3Al_2O_3 \cdot 5P_2O_5 \cdot 26H_2O$ and that deviations of natural taranakite from this may be referred to impurities. It appears that possibilities of substitution are numerous and that this fact has been overlooked by most previous workers.

	Taranakite from pit	*Taranakite from breccia*
K_2O	5.9	8.9
Na_2O	0.1	t
$(NH_4)_2O$	1.8	0.8
CaO	0.6	0.4
Fe_2O_3	1.7	0.8
Al_2O_3	17.0	19.5
P_2O_5	38.9	38.4
H_2O	34.9	30.3
Rem. (Insol.)	1.3	0.6
	102.2	99.7

Analyst: John Murray

Spectrographic analyses showed the presence also of Ag, Cu, Ga, Mn, Mg, Pb, Si, and Ni. X-ray data are presented at top of the next page. Thermal data:[2] The heating curve for taranakite is presented (Fig. 2).

Taranakite exists until part of its water is given off, the reaction that is manifest by the first endothermic peak; T_1 has an x-ray pattern similar to that of the lower hydrate as reported upon by Haseman *et al.* (5); after the next endothermic reaction, apparently dependent upon the loss of the remaining water, product T_2 is obtained—this product is amorphous to x-rays; the exothermic reaction appears to represent an irreversible (according to the cooling curve) reconstructive inversion of T_2 to product T_3; T_3 is changed to T_4 as the result of the endothermic reaction near the end of the heating curve. X-ray data obtained for T_3 and T_4 do not correlate with any published patterns. Perhaps, although chemical analyses of the product do not corroborate this, this last reaction represents a loss of part of the phosphorus. The position of the end of the curve may represent the beginning of another reaction or merely a difference in conductivity of material T_4 from that of T_3.

GENESIS

It has been reported that brushite is "Widespread in small amounts in insular and continental phosphate deposits. [and] Frequently occurs

[2] Differential thermal analysis equipment used was the same as that used for the brushite.

X-ray data:

X-ray setup used was same as that for brushite. Further, diffraction patterns of taranakite from Pig Hole Cave and those of minervite from Cesse, Grotto De Minerva, France (U. S. National Museum specimen number *R5531*) as obtained by using a 114.6 mm. Philips camera and Cu Kα radiation, were compared and found to be essentially equal.

d, Å	I, approx. counts	d, Å	I, approx. counts
15.49	3250	1.92	15
7.82	750	1.90	60
7.43	570	1.88	25
7.13	190	1.86	40
5.82	420	1.84	20
5.01	140	1.83	15
4.62	110	1.82	50
4.27	390	1.79	55
4.15	60	1.77	40
4.00	110	1.75	15
3.79	800	1.74	25
3.72	350	1.71	60
3.57	500	1.68	45
3.34	300	1.65	15
3.27	320	1.64	55
3.16	300	1.62	30
3.12	620	1.61	35
3.06	30	1.593	20
2.94	140	1.588	20
2.83	390	1.57	15
2.81	400	1.52	15
2.73	250	1.50	15
2.70	90	1.48	25
2.62	430	1.47	15
2.55	90	1.42	50
2.53	70	1.39	20
2.48	40	1.35	20
2.44	20	1.33	25
2.38	230	1.32	15
2.34	50	1.313	20
2.26	90	1.312	20
2.17	50	1.28	35
2.14	50	1.23	25
2.12	35	1.22	25
2.09	80	1.20	25
2.06	150	1.17	20
2.00	15	1.12	20
1.96	60	1.11	15

(88 degrees 2θ end of scan)

as an incrustation upon ancient human and animal bones and has been observed in human urinary calculi" (8). It might be suggested that the shapes of the masses of crystals in the guano pit at Pig Hole Cave
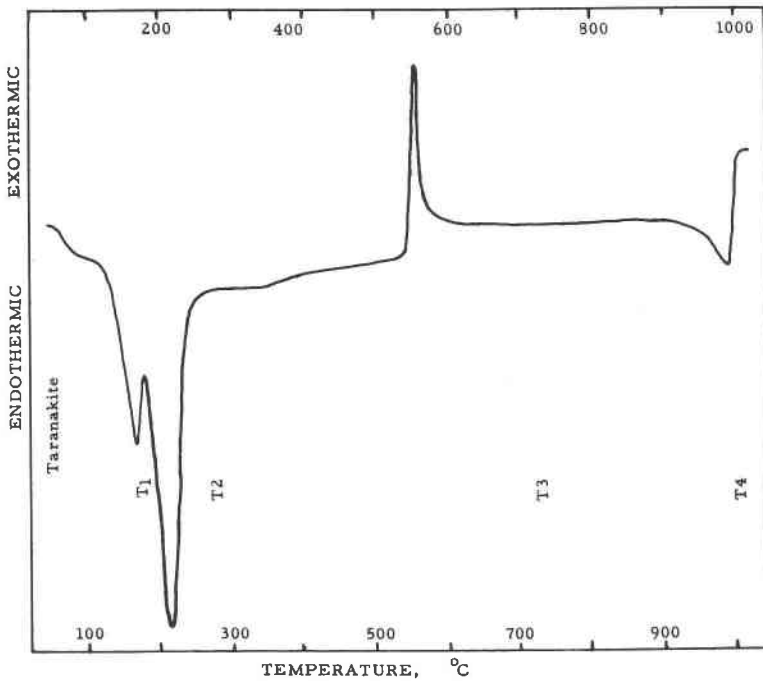
Fɪɢ. 2. Tracing of thermal (*D.T.A.*) curve of taranakite.

indicate that the brushite here represents former bones included in the deposit. Although this does not appear to be likely to the writers, it admittedly has not been possible to prove or disprove the possibility. That this occurrence is in a perennially damp location just as are most of the previously reported occurrences, appears to indicate this condition to be a major control. Other than this, only the possible role(s) of the decaying of the bat hair along with the decaying guano appears to offer anything new concerning the origin of brushite.

The occurrences of the taranakite in the brecciated clay and within the bat guano deposit in the zone adjacent to the bottom clay plus the composition of it and of each of these materials suggest that the taranakite was formed by interactions between the bat guano (and possibly the bat hair) and the clay. If this origin did obtain, at least most of the aluminum would have been derived from the clay and the potassium and phosphorus from the guano and/or hair. This appears to be possible considering the composition of clay minerals, of bat guano, and of bat hair.

This suggested origin appears to be corroborated by the work of Gautier (3) and by the recent investigations of numerous soil scientists,

for example, Haseman *et al.* (4) Gautier showed that in nitrogenous material of animal origin most of the phosphorus is retained as $(NH_4)_2HPO_4$ and that this can react with argillaceous or calcareous material to produce phosphates of aluminum or calcium. Haseman, *et al.* showed, that in conjunction with phosphate fixation by soil minerals (mainly clays) that aluminum phosphates are the end products of the phosphate-induced decomposition of kaolinite. Further, Kittrick and Jackson (7) reported that they were able, by using an electron microscope, to observe during the process the actual progressive formation of different aluminum phosphate crystals concomitantly with the decomposition of kaolinite crystals. It is perhaps of special interest that "Taranakite-like crystals" formed in one of their experiments (apparently the Na-analogue of taranakite according to the formula they give). As the result of their observations, these last two workers concluded that "It can be seen then that the formation of aluminum phosphates at the expense of kaolinite is a solution-precipitation phenomenon involving dissociation of aluminum from the kaolinite crystal, which is in accord with the aluminum-dissociation and solubility product principles advanced . . . to explain phosphate fixation by soil minerals."

Apparently the main control is that taranakite (and other minerals such as leucophosphite and minyulite) must form in the presence of an excess of the proper alkali ion—otherwise the alkali will be lost and varisite (or related strengite or barrandite) will form (1, 5). A further control appears to be the constant or nearly constant presence of water (at least dampness)—Hutchinson (2) noted that the mineral has been found only in areas that are perennially damp; the Pig Hole Cave occurrence is no exception.

Because of the likelihood that at least most of the aluminum of the taranakite was derived from the clay, *x*-ray and differential thermal analyses were made of the brecciated clay associated with the taranakite in order to determine if the clay of the fragments showed evidences of any changes in composition near their contacts with the taranakite. Samples from the zones within approximately one millimeter of the contact (hereinafter referred to as "*O*" for outer) and samples from the part of the breccia fragments farthest from the taranakite (hereinafter referred to as "*I*" for inner) were analyzed. The analyses showed the *O* sample to have no kaolinite whereas the *I* sample does contain some; illite appears to be better crystallized in the *I* sample than in the *O* sample; quartz appears to make up a slightly greater percentage of sample *O* than of sample *I*; vermiculite(?) is present in only the *O* material; analyses of ethylene glycol-saturated samples of each material indicate that they both contain minor amounts of halloysite. These data suggest that under

the conditions prevalent at the locality when the taranakite was formed, *i.e.*, when there was a presence of phosphate solutions, that aluminum was more readily available from kaolinite than from illite. Apparently, while the illite started to break down, and in part perhaps did break down to vermiculite—thus arresting further release of aluminum, kaolinite broke down completely thus releasing its aluminum for formation of aluminum phosphates. There also is the possibility, however, that these processes did not occur as direct consequences of the special conditions set up in the cave but rather that they occurred because of more or less normal weathering in which case the above noted relationships might not pertain to the problem at all. This alternative is suggested by the recent findings of Rich and Obenshain (9, and Rich, personal communication) who have reported similar relationships to occur in a Virginia soil. They report that from the surface downward that kaolinite content increases, illite content (and degree of crystallization) increases, and dioctahedral vermiculite content decreases.

One other fact concerning taranakite warrants further investigation because of its possible relation to genesis of the mineral. Hutchinson (2) noted that in his spectrographic analysis of minervite that along with many other elements, Pb was present. He noted that the lead might be a contaminant. The spectrographic analyses made in conjunction with this investigation also showed, along with many other elements, Pb. In fact, Pb was the only element that occurred in the taranakite that was not found to occur in either the guano or the adjacent clay. There appears to be no way in which the taranakite collected and analyzed by the writers could have been contaminated. It therefore appears that an affinity must exist between lead and the taranakite lattice. Perhaps the correct answer is that suggested in a later publication by Hutchinson (6) *i.e.*, " . . .minute amounts of Pb^{++} ($r = 1.32$ Å) may conceivably replace K^+ ($r = 1.33$ Å) in the mineral." It appears quite possible that such a substitution could occur in conjunction with one or more of the substitutions suggested as possible by the tentative formula for taranakite given here.

aided in their laboratories. J. J. Glass of the Geochemistry and Petrology Branch of the U. S. Geological Survey checked all of the optical data for brushite and some of the data for taranakite. George Switzer of the U. S. National Museum and B. W. Nelson of the Department of Geological Sciences at Virginia Polytechnic Institute critically read the manuscript. The writers gratefully acknowledge all these contributions.

References

1. Axelrod, J. M., Carron, M. K., Milton, Charles, and Thayer, T. P., Phosphate mineralization at Bomi Hill and Bambuta, Liberia, West Africa: *Am. Mineral.*, **37**, 883–909 (1952).

2. Bannister, F. A., and Hutchinson, G. E., The identity of minervite and palmerite with taranakite: *Mineral. Mag.*, **28**, 31–35 (1947).

3. Gauthier, A., Minervite and the gneisses phosphorite: *Bull. Soc. Chim.*, **15**, 533–540 (1913).

4. Haseman, J. F., Brown, E. H., and Whitt, C. D., Some reactions of phosphate with clays and hydrous oxides of iron and aluminum: *Soil Science*, **70**, 257–271 (1950).

5. Haseman, J. F., Lehr, J. R., Jr., and Smith, J. P., Mineralogical character of some iron and aluminum phosphates containing potassium and ammonium: *Soil Science Soc. Am. Proc.*, **15**, 76–84 (1950).

6. Hutchinson, G. E., Survey of contemporary knowledge of biochemistry, pt. 3, The biogeochemistry of vertebrate excretion: *Bull. Am. Mus. Nat. Hist.*, **96**, 480 (1950).

7. Kittrick, J. A., and Jackson, M. L., Electron microscope observations of the formation of aluminum phosphate crystals with kaolinite as the source of aluminum: *Science*, **120**, 508–509 (1954).

8. Palache, Charles, Berman, Harry, and Frondel, Clifford, The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana, Vol. 2, seventh edit.: Wiley, New York, 704–706 and 999–1000 (1951).

9. Rich, C. I., and Obenshain, S. S., Chemical and clay mineral properties of the red-yellow podzolic soil derived from muscovite schist: *Soil Science Soc. Am. Proc.*, **19**, 334–339 (1955).

10. Sekanina, Josef, Nález Brushitu na Kostech ze Starého Bítova na Vranovské Přehradě: *Publ. Fac. Sci. Univ. Masaryk, Brno*, **220**, 1–12 (1935).