

THE MAGNESIUM PHOSPHATES HANNAYITE,
SCHERTELITE AND BOBIERRITEA. WILLIAM FRAZIER, JAMES R. LEHR AND JAMES P. SMITH,
*Division of Chemical Development, Tennessee Valley
Authority, Wilson Dam, Alabama.*

ABSTRACT

Synthetic hannayite, $\text{Mg}_3(\text{NH}_4)_2\text{H}_4(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$, was prepared as coarse euhedrons. Its morphology is similar to that described by Goldschmidt, but its optical properties differ from those reported, with reservations, by Larsen. Hannayite is triclinic, biaxial (-); $\alpha = 1.504 \pm 0.002$, $\beta = 1.522 \pm 0.002$, $\gamma = 1.539 \pm 0.002$; $2V$ nearly 90° (calc. 87°); $r < v$ weak. The space group is $P\bar{1}$; $a = 7.70 \text{ \AA}$, $b = 11.51 \text{ \AA}$, $c = 6.70 \text{ \AA}$; $\alpha = 76.0^\circ$, $\beta = 99.8^\circ$, $\gamma = 115.8^\circ$; cell contains one formula weight; measured density 2.03 ± 0.02 , calc. 2.03. The morphological c of Goldschmidt's cell and the c derived from x -ray data coincide, but the selections of a and b differ.

Schertelite, $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, has not been described, except for its composition. Schertelite and hannayite are formed under similar conditions, but schertelite is less stable in water or on exposure to the atmosphere. Schertelite is orthorhombic, biaxial (+); $\alpha = 1.508 \pm 0.002$, $\beta = 1.515 \pm 0.002$, $\gamma = 1.523 \pm 0.002$; $2V$ nearly 90° (calc. 86°); $\alpha = b$, $\beta = c$, $\gamma = a$ of the x -ray cell. The space group is $D_{2h}^{16} - Pbc_a$; $a = 11.47 \text{ \AA}$, $b = 23.63 \text{ \AA}$, $c = 8.62 \text{ \AA}$; cell contents $8[\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$, density (calc.) 1.83.

Synthetic bobierrite, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, differs only slightly from the mineral varieties and has $\alpha = 1.501 \pm 0.002$, $\beta = 1.513 \pm 0.002$, $\gamma = 1.536 \pm 0.002$; $2V$ large (calc. 73°); $Z \wedge c = 24.5^\circ$. The strongest x -ray lines are: 6.96 \AA (100), 2.94 \AA (27), 8.04 \AA (18), and 2.81 \AA (13).

Hannayite and schertelite are formed in concentrated ammonium phosphate solutions, whereas struvite and newberyite are formed in dilute solutions. Both hannayite and schertelite alter hydrolytically to mixtures of struvite and schertelite. In water, struvite alters slowly to $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ and then to the more stable bobierrite.

INTRODUCTION

In studies of the system $\text{MgO}-(\text{NH}_4)_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ between the regions of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite) and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite), well-crystallized hannayite, schertelite, and bobierrite of high purity were prepared. Materials examined to determine the crystallographic studies were prepared from solutions to which acetate was added to increase the size and improve the shape of the crystals.

The morphology of hannayite was described from goniometric measurements by Goldschmidt (1918), but the x -ray unit-cell constants have not been reported. Optical properties ascribed, with reservations, to hannayite by Larsen (1921) appear to be erroneous. The literature contains virtually no description of schertelite. On the other hand, the crystallography of bobierrite is well established (Palache *et al.*, 1951), but the optical properties of laboratory preparations of this compound differ significantly from those reported for the impure mineral.

HANNAYITE

Preparation. Hannayite, $Mg_3(NH_4)_2H_4(PO_4)_4 \cdot 8H_2O$, crystallized at 25° C. when 4.3 grams of magnesium acetate was added to a solution of 32.2 grams of $NH_4H_2PO_4$ and 3.1 grams of $NH_4C_2H_3O_2$ in 100 ml of water. Coarse triclinic euhedrons of hannayite with the habit described by Gold-

TABLE 1. X-RAY POWDER DIFFRACTION DATA. $CuK\alpha=1.5405 \text{ \AA}$

Hannayite				Schertelite				Bobierrite			
d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d ¹	I/I ₁
10.27	0.11	2.55	0.03	5.94	1.00	2.31	0.04	8.04	0.18	7.7	0.24
6.96	1.00	2.53	0.05	5.75	0.11	2.24	0.05	6.96	1.00	6.7	1.00
5.98	0.03	2.49	0.02	5.60	0.08	2.21	0.05	4.87	0.02		
5.34	0.06	2.43	0.06	5.21	0.37	2.19	0.05	4.19	0.05		
5.15	0.28	2.37	0.10	4.87	0.06	2.11	0.04	4.11	0.03		
4.90	0.03	2.31	0.02	4.50	0.07	2.09	0.02	4.00	0.03		
4.64	0.23	2.25	0.08	4.44	0.05	2.07	0.02	3.81	0.02		
4.53	0.03	2.19	0.12	4.31	0.19	2.03	0.03	3.48	0.08		
4.00	0.04	2.07	0.07	4.13	0.01	1.98	0.01	3.16	0.04	3.19	0.08
3.85	0.04	2.04	0.05	3.98	0.04	1.96	0.02	3.02	0.10		
3.75	0.18	2.00	0.03	3.91	0.19	1.93	0.02	2.94	0.27	2.94	0.32
3.66	0.13	1.96	0.03	3.74	0.02	1.91	0.03	2.81	0.13	2.69	0.32
3.60	0.05	1.93	0.02	3.60	0.10	1.90	0.02	2.66	0.03		
3.46	0.73	1.92	0.02	3.46	0.21	1.88	0.02	2.61	0.06		
3.29	0.22	1.89	0.05	3.44	0.11	1.86	0.04	2.57	0.09	2.51	0.24
3.22	0.10	1.87	0.02	3.36	0.11	1.83	0.02	2.41	0.12	2.40	0.16
3.18	0.09	1.83	0.02	3.02	0.22	1.80	0.02	2.35	0.03		
3.13	0.14	1.74	0.07	2.97	0.43	1.79	0.02	2.30	0.02		
3.00	0.15	1.71	0.01	2.86	0.05	1.77	0.03	2.26	0.02	2.20	0.08
2.93	0.09	1.69	0.02	2.80	0.29	1.76	0.03	2.13	0.10		
2.90	0.05	1.66	0.01	2.71	0.03	1.74	0.03	2.11	0.05		
2.81	0.02	1.65	0.02	2.63	0.09	1.71	0.06	2.06	0.03	2.05	0.08
2.78	0.03	1.62	0.02	2.58	0.17	1.65	0.02	1.94	0.03		
2.69	0.02	1.60	0.05	2.52	0.03	1.61	0.06	1.92	0.02		
2.66	0.11	1.54	0.02	2.46	0.10	1.56	0.02	1.90	0.03		
2.59	0.02			2.39	0.08	1.54	0.03	1.87	0.04		
				2.37	0.05			1.74	0.02		
								1.69	0.02		
								1.67	0.03	1.66	0.08
								1.65	0.02		
								1.62	0.01		
								1.60	0.02		
								1.58	0.01		
								1.56	0.01	1.57	0.08
								1.51	0.02		

¹ Data for $Mg_3(PO_4)_2 \cdot 8H_2O$ (ASTM 214, First Set), No reference; Hanawalt files.

schmidt (Palache *et al.*, 1951) were prepared at 100° C. by slow addition without stirring of 5 grams of magnesium acetate to a solution of 150 grams of $\text{NH}_4\text{H}_2\text{PO}_4$ and 10 grams of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 100 ml of water. Compositions of typical preparations of hannayite are shown in the tabulation.

	1	2	$\text{Mg}_3(\text{NH}_4)_2\text{H}_4(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$, stoichiometric
MgO	19.06	19.00	18.98
$(\text{NH}_4)_2\text{O}$	8.10	8.00	8.17
P_2O_5	44.49	44.39	44.58
H_2O	28.35	28.61	28.27

X-ray studies. X-ray powder diffraction data were obtained with a Norelco high-angle goniometer and CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$) as listed in Table 1.

Single-crystal *x*-ray studies were made on selected flawless, clear prisms with the habit reported by Goldschmidt (Palache *et al.*, 1951). Lattice constants were determined from a single setting. A rotation photograph, zero, first, and second layer-line Weissenberg photographs, and a composite zero and first layer-line Weissenberg photograph were taken about the *c* axis. In accordance with the consistently holohedral symmetry observed in some 50 preparations, the most probable space group is $P\bar{1}$. On the assumption of one formula weight per unit cell, the calculated density is 2.03. The dimensions of the triclinic unit cell are $a = 7.70 \text{ \AA}$, $b = 11.51 \text{ \AA}$, $c = 6.70 \text{ \AA}$, $\alpha = 76.0^\circ$, $\beta = 99.8^\circ$ and $\gamma = 115.8^\circ$. The morphological *c* of Goldschmidt's cell and the *c* derived from *x*-ray measurements coincide, but the selections of *a* and *b* differ.

Crystal morphology. As indexed on the *x*-ray cell, the principal forms are $\{100\}$, $\{010\}$, $\{110\}$, $\{001\}$, $\{01\bar{1}\}$, and $\{\bar{1}11\}$. Crystals are tabular $\{100\}$ with prominent $\{01\bar{1}\}$, modified by narrow $\{110\}$, and elongate along *c*. The apparent equivalence between Goldschmidt's morphological forms and ours is shown in the tabulation.

	Goldschmidt cell	X-ray cell
a	(100)	($\bar{1}10$)
m	(110)	($\bar{1}00$)
M	($\bar{1}\bar{1}0$)	(0 $\bar{1}0$)
ω	($\bar{1}33$) ($133?$)	(0 $\bar{1}\bar{1}$)
c	(001)	($\bar{1}11$)

It has not been possible to derive a simple unambiguous transformation from our *x*-ray cell to Goldschmidt's goniometric cell ($\alpha = 122^\circ 31'$, $\beta = 126^\circ 46'$, $\gamma = 54^\circ 09'$, $a:b:c = 0.699:1:0.974$). Comparison of the mor-

phology, crystal habit, and chemical composition of our preparations with those described by Goldschmidt, however, shows that the two descriptions refer to the same species.

In selecting crystals for goniometric and x -ray studies, we observed that slowly grown {100} tablets of hannayite tend to develop faces that are non-parallel and sometimes show curvature because of vicinal terraces. This imperfection increases with increase in crystal size. For our studies we selected only crystals that were optically clear prisms of nearly perfect geometric form. Related pairs of crystal faces were coplanar and free from terraces, curvature, and vicinal areas.

Optical data. The synthetic crystals were biaxial (—), with $2V$ nearly 90° (calc. 87°). The indices of refraction (N_D^{25}) were $\alpha = 1.504 \pm 0.002$, $\beta = 1.522 \pm 0.002$, and $\gamma = 1.539 \pm 0.002$. Dispersion ($r < v$) was weak. The orientation of the optic plane coincided very closely with $\bar{2}21$ of the x -ray cell, and the Bx_0 was nearly normal to {110}. The density calculated by the Gladstone-Dale relationship (Larsen and Berman, 1934) was 2.00; that determined with heavy liquids was 2.03.

The optical data reported by Larsen (Palache *et al.*, 1951) do not appear to apply to the mineral hannayite. We cannot reconcile his optical description with our preparations, and the indices of refraction he reported are well above those of all the magnesium ammonium phosphates we have encountered. His values also yield the high value of 2.18 for the density calculated by the Gladstone-Dale relationship

SCHERTELITE

Schertelite, $Mg(NH_4)_2H_2(PO_4)_2 \cdot 4H_2O$, is reported (Palache *et al.*, 1951) to occur in association with struvite, hannayite and newberyite, but its crystallographic properties are not described in the literature.

Preparation. Schertelite is formed under conditions similar to those for the preparation of hannayite, but schertelite is much more soluble and is obtained from solutions of higher magnesium content. It was prepared as coarse prismatic euhedrons at 25° C. by adding 8.6 grams of magnesium acetate to a solution of 32.2 grams of $NH_4H_2PO_4$ and 3.1 grams of $NH_4C_2H_3O_2$ in 100 ml of water. Schertelite was also prepared at 100° C. by the method of preparation of hannayite at that temperature by extending the equilibration time for several days. The initially formed hannayite slowly dissolved, and well-formed coarse prisms and tablets of schertelite crystallized. Compositions of washed, acetone-rinsed, and air-dried crystals of schertelite are shown in the tabulation.

	1	2	Mg(NH ₄) ₂ H ₂ (PO ₄) ₂ ·4H ₂ O, stoichiometric
MgO	12.73	12.70	12.43
(NH ₄) ₂ O	15.40	15.70	16.04
P ₂ O ₅	43.43	43.23	43.76
H ₂ O	28.44	28.37	27.77

Schertelite dissolves rapidly and incongruently in water with the formation of struvite. Exposure of schertelite to the atmosphere for several months results in alteration of the surface of the crystals, apparently to an intimate mixture of struvite and monoammonium phosphate. The composition of the alteration product was deduced from chemical knowledge of the reactions of schertelite; the colloidal particles of the alteration product could not be identified by petrographic or *x*-ray examination.

Morphology. Schertelite crystals have orthorhombic symmetry, class *mmm* and display several habits. They usually develop as single stout rods elongated along *c*, with prominent {110} and {111} and modifying {100} and {010}. Slowly grown crystals tend to be tabular {100}, with nearly equally developed {010}, {001}, {111}, and {110}. The indexing of the forms is based on the *x*-ray cell, with $\alpha = b$, $\beta = c$ and $\gamma = a$. No prominent cleavages were observed.

Optical data. Crystals of schertelite are biaxial (+), with 2*V* very close to 90° (calc. 86°). The indices of refraction (*N_D²⁵*) are $\alpha = 1.508 \pm 0.002$, $\beta = 1.515 \pm 0.002$ and $\gamma = 1.523 \pm 0.002$. The optic plane is {001}, with $\gamma(\text{Bx}_a) = a$. The density calculated from the Gladstone-Dale relationship is 1.82.

X-ray data. The *x*-ray powder diffraction data are listed in Table 1. Rotation and Weissenberg photographs were made of selected equant colorless prisms. In the orthorhombic unit cell $a = 11.47 \text{ \AA}$, $b = 23.63 \text{ \AA}$, and $c = 8.62 \text{ \AA}$. The most probable space group is *D*_{2h}¹⁶—*Pbca*. The unit cell contains 8[Mg(NH₄)₂H₂(PO₄)₂·4H₂O], for which the calculated density is 1.83.

BOBIERRITE

The mineral bobierite has been described in considerable detail (Palache *et al.*, 1951), but no example of the pure end member, Mg₃(PO₄)₂·8H₂O, is included in the descriptions. Stout monoclinic blades of bobierite with the habit and morphology described by Barth (1937) were obtained when Mg₃(PO₄)₂·22H₂O was allowed to stand in water at 25° C.

for about 2 months. A similar preparation was reported by Bassett and Bedwell (1933). The composition of a typical preparation of air-dried bobierrite is shown in the tabulation.

	1	Mg ₃ (PO ₄) ₂ ·8H ₂ O, stoichiometric
MgO	29.61	29.72
P ₂ O ₅	34.47	34.87
H ₂ O	35.92	35.41

The optical properties of laboratory preparations of bobierrite differ slightly from those reported for the mineral (Palache *et al.*, 1951), and approach those reported for a mineral from Minnesota (Gruner and Stauffer, 1943). The indices of refraction N_D^{25} of our preparations are $\alpha = 1.501 \pm 0.002$, $\beta = 1.513 \pm 0.002$ and $\gamma = 1.536 \pm 0.002$; the calculated $2V$ is 73° . On $\{010\}$, $Z \wedge c = 24.5^\circ$, instead of 29° as reported for two mineral specimens.

X-ray powder diffraction data for bobierrite are listed in Table 1. The data agree with and extend considerably the published data (ASTM 214, First Set).

CHEMICAL RELATIONSHIPS

Hannayite, schertelite, bobierrite, newberyite and struvite are reported to be commonly associated minerals, particularly in guano deposits. These mixtures may be formed by reaction of magnesium with concentrated ammonium phosphate solutions of the guano deposit followed by alterations in the course of leaching and aeration of the deposits.

In laboratory preparations, hannayite and schertelite precipitate rapidly from concentrated solutions of ammonium phosphate over the pH range 3.5 to 6 and the temperature range 25° to 100° C. Newberyite or struvite, depending on the pH, is formed at lower concentrations of ammonium phosphate. When either newberyite or struvite is placed in a saturated solution of monoammonium phosphate, it is replaced by hannayite, which then alters to schertelite in a few days.

The magnesium ammonium phosphates undergo hydrolytic alteration in water and in very dilute solutions of magnesium, ammonium, and phosphate ions. Schertelite, which is reported to occur sparingly in drier layers of guano, dissolves rapidly and incongruently in water to form struvite. Hannayite also dissolves incongruently in water, but more slowly than schertelite, and is replaced by a mixture of newberyite and struvite in less than a week at 25° C. On standing in water in an open container, struvite is slowly replaced by the triclinic $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ which is then replaced by the more stable octahydrate, bobierrite, in

about two months. Bassett and Bedwell (1933) reported that this conversion required about two weeks. Taylor (1963) has determined the solubility relationships of struvite, bobierite, newberyite, and $Mg_3(PO_4)_2 \cdot 22H_2O$.

Guano is a heterogeneous material that undergoes changes resulting from losses of ammonia by aeration and nitrification, from removal of ammonium phosphate from solution by precipitation reactions, and from extraction of soluble constituents by leaching. The chemical alterations observed in the laboratory explain the complex, non-equilibrium mixtures of the magnesium phosphates in guano and similar deposits. Because of the ease with which some of the hydrolytic alterations occur, considerable care should be exercised in the collection and storage of magnesium ammonium phosphates intended for mineralogical characterization.

REFERENCES

- BARTH, T. F. W. (1937) Crystallographic studies in the vivianite group. *Am. Mineral.* **22**, 325-341.
- BASSETT, H. AND W. L. BEDWELL (1933) Studies of phosphates. Part II. Orthophosphates of the type $M_3(PO_4)_2 \cdot xH_2O$, *Jour. Chem. Soc.* 871-876.
- GOLDSCHMIDT, VICTOR (1918) *Atlas der Krystallformen*, vol. 4, Heidelberg.
- GRUNER, J. W. AND C. R. STAUFFER (1943) A unique occurrence of bobierite, $Mg_3(PO_4)_2 \cdot 8H_2O$. *Am. Mineral.* **28**, 339-340.
- LARSEN, E. S. (1921) The microscopic determination of non-opaque minerals. *U. S. Geol. Surv. Bull.* **679**.
- AND H. BERMAN (1934) The microscopic determination of non-opaque minerals, 2nd ed., *U. S. Geol. Surv. Bull.* **848**.
- PALACHE, C., H. BERMAN AND C. FRONDEL (1951) *Dana's System of Mineralogy*, vol. II, John Wiley & Sons, New York.
- TAYLOR, A. W., A. W. FRAZIER, E. L. GURNEY AND J. P. SMITH (1963) Solubility products of di- and trimagnesium phosphates and the dissociation of phosphate solutions. *Trans. Faraday Soc.* **59** (in press).

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