

X-RAY STUDIES OF ALUMINUM AND IRON PHOSPHATES
CONTAINING POTASSIUM OR AMMONIUMJAMES P. SMITH AND WALTER E. BROWN, *Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Alabama.*

ABSTRACT

Lattice constants and space groups are reported for several complex iron and aluminum phosphates containing potassium or ammonium: $H_6(K, NH_4)_3Al_5(PO_4)_8 \cdot 18H_2O$ (taranakite), $H_2(K, NH_4)(Al, Fe)(PO_4)_2 \cdot H_2O$, $H_2(K, NH_4)(Al, Fe)(PO_4)_2$, $(K, NH_4)(Al, Fe)_2(PO_4)_2(OH) \cdot 2H_2O$ (leucophosphite) and $H_8(K, NH_4)(Al, Fe)_3(PO_4)_6 \cdot 6H_2O$. A new formula given for taranakite is consistent with the chemical composition, density and space-group requirements. In a layer structure postulated for taranakite, aluminum phosphate sheets are separated by water molecules.

INTRODUCTION

An interest in phosphate-soil relations led Haseman *et al.* (1950, 1951) to the preparation of several groups of complex iron and aluminum phosphates from reagent chemicals or through treatment of soil minerals with phosphate solutions. Their work included determinations of the chemical compositions, optical properties and *x*-ray powder diffraction spacings of the compounds, three of which have been shown to be identical with the minerals taranakite (Haseman, *et al.*, 1950), minyulite (Haseman *et al.*, 1951) and leucophosphite (Axelrod *et al.*, 1952).

Single-crystal *x*-ray studies of representative members of these groups of compounds are reported here. To facilitate cross reference, Haseman's designations of compounds are included.

X-RAY MEASUREMENTS

The results of the *x*-ray studies* are summarized in Table 1. Densities were calculated on the basis of theoretical chemical compositions instead of those obtained by chemical analyses.

Taranakite, $H_6(K, NH_4)_3Al_5(PO_4)_8 \cdot 18H_2O$ (Group 1, Product A)

Bannister and Hutchinson (1947) concluded that the minerals minerite, palmerite and taranakite are identical and on the basis of priority should be called taranakite. A synthetic mineral obtained upon treatment of kaolinite with potassium phosphate solution at 50° C. was assumed by Stout (1940) to be a product of the exchange of phosphate ions for hydroxyl ions of the kaolinite lattice. The mineral was shown by

* Diameter of Weissenberg camera, 57.3 mm. Filtered copper radiation ($\lambda=1.541 \text{ \AA}$) used for aluminum compounds—filtered iron radiation ($\lambda=1.936 \text{ \AA}$) for iron compounds. With the exception noted, diffraction data were obtained from at least two axial settings of the crystals. Where possible, reciprocal angles were determined by the method of triangulation (Buerger, 1942). Axial measurements are considered reliable to $\pm 0.3\%$ —interaxial angles to $\pm 20'$.

TABLE 1. LATTICE CONSTANTS OF SYNTHETIC IRON AND ALUMINUM PHOSPHATES CONTAINING POTASSIUM OR AMMONIUM IONS

Designation*	Unit-Cell Contents	Crystal System	Probable Space Group	Lattice Constants			Density, g./cc.		
				a	b	c	β	X-Ray	Pycnometric
1 A	6[H ₆ K ₃ Al ₃ (PO ₄) ₈ · 18H ₂ O]	Hexagonal (rhombohedral)	C _{3h} ⁶ or D _{3d} ⁶	8.71	—	96.1	—	2.11	2.09
2 C	8[H ₂ KAl(PO ₄) ₂ · H ₂ O]	Monoclinic	C _{2h} ⁶ —P2 ₁ /c	10.04	9.10	16.34	101°18'	2.49	2.52
2 D	8[H ₂ KFe(PO ₄) ₂ · H ₂ O]	Monoclinic	C _{2h} ⁶ —P2 ₁ /c	10.22	9.23	16.56	99°20'	2.61	2.63
3 E	3[H ₂ KFe(PO ₄) ₂]	Triclinic	C ₁ ¹ or C ₁ ¹	9.26	9.49	7.20	—†	2.87	2.90
4 I	4[(KF ₂ (PO ₄) ₂ (OH) · 2H ₂ O)]	Monoclinic	C _{2h} ⁶ —P2 ₁ /#	9.76	9.65	9.70	102°54'	2.92	2.93
4 J	4[(NH ₄)Al ₃ (PO ₄) ₂ (OH) · 2H ₂ O]	Monoclinic	C _{2h} ⁶ —P2 ₁ /#	9.63	9.59	9.58	103°19'	2.42	—
5 —	2[(H ₈ (NH ₄)Al ₇ (PO ₄) ₆ · 6H ₂ O]	Hexagonal	D _{6h} ⁴ , C _{6h} ⁴ , D _{3h} ⁴	8.90	—	16.50	—	2.29	—
5 K	2[H ₈ (NH ₄)Fe ₃ (PO ₄) ₆ · 6H ₂ O]	Hexagonal	D _{6h} ⁴ , C _{6h} ⁴ , D _{3h} ⁴	9.14	—	16.88	—	2.36	2.36

* Haseman *et al.* (1951).

† α = 110°11' *et al.*, β = 117°7', γ = 97°56'.

Low and Black (1948), however, to be a complex aluminum phosphate. Haseman *et al.* (1951) grew tarankite crystals as single hexagonal plates or as stacks of plates resembling kaolinite worms, too small to give good interference figures. The crystals appeared to be biaxial and were reported to be monoclinic.

A redetermination of the optical and morphological properties showed the crystals to be uniaxial negative (see also Murray and Dietrich, 1956). The uniaxial character and the alternate undercut-overcut $\{10\bar{1}1\}$ lateral faces of the plates are clearly consistent with the rhombohedral symmetry indicated by the *x*-ray study. The observed reflections conform to the conditions $hk\bar{l}$ present when $-h+k+l=3n$, $hh2\bar{h}l$ present when $l=3n$, and $h\bar{h}0l$ present when $h+l=3n$ and $l=2n$, which are characteristic of the space groups C_{3v}^6-R3c and $D_{3d}^6-R\bar{3}c$.

The empirical formula $H_4K_2Al_3(PO_4)_5 \cdot 11H_2O$, reported by Haseman *et al.* (1951) from chemical analyses, and the space-group multiplicities lead to density values of 2.61 and 1.30, which differ greatly from the pycnometric value, 2.09. An alternative formula, $H_6K_3Al_5(PO_4)_8 \cdot 18H_2O$, agrees equally well with the chemical analyses, gives a density of 2.11, and is considered to be a more probable formula for taranakite.

A lower hydrate (group 1, product B), obtained at 95° C., has the empirical composition $H_6K_3Al_5(PO_4)_8 \cdot 13H_2O$. Crystals in sizes suitable for single-crystal *x*-ray study were not obtained. The powder diffraction pattern has an intense line at 13.8 Å. One preparation contained relatively large crystals which individually comprised both hydrates. The diffraction pattern revealed that the plane giving rise to the 13.8 Å spacing of the lower hydrate is parallel to that giving rise to the 16.0 Å spacing of the higher hydrate. This is known to be the 006 reflection in the higher hydrate. Certain lines, identified as the *h*00 reflections of the higher hydrate, are common to diffraction patterns of both hydrates. Apparently, the unit-cell dimensions of the two hydrates are the same in the *a* direction and the cell shrinks in the *c* direction on loss of water. This is consistent with a view that taranakite has a layer structure with water molecules disposed between sheets comprising aluminum, phosphate, and perhaps potassium or ammonium ions, there being six such layers in a unit cell normal to the *c* axis. The platy habit and the greater increase in the refractive index normal to the plate than in the index parallel to the plate on dehydration are also in accord with this view.

The portion of a given layer lying in one unit cell contains five aluminum atoms and eight phosphorus atoms. The space-group multiplicities are such that at least two of the five aluminum atoms and at least two of the eight phosphorus atoms must lie in special positions. These conditions, along with the possibility of close packing of oxygens and the usual spatial restrictions on the coordination of oxygens by aluminum and phos-

phorus atoms, indicate that a trial-and-error approach to the crystal structure may be practical, once a choice can be made between the two space groups.

$H_2(K, NH_4)(Al, Fe)(PO_4)_2 \cdot H_2O$ (Group 2, Products C and D)

The synthetic minerals of group 2 have a tabular prismatic form and monoclinic symmetry. Their natural occurrence has not been reported. All four end members of the series were prepared, but only two, the potassium aluminum and the potassium iron combinations, were studied by single-crystal methods. The observed reflections for both materials conformed to the conditions hkl present in all orders, $h0l$ present when $l=2n$, and $0k0$ present when $k=2n$. The most probable space group is $C_{2h}^5-P2_1/c$.

The equatorial Weissenberg photograph for the c -axis rotation displayed a pseudo-hexagonal symmetry that was lacking in the photographs of higher levels. This suggests that the crystal structure, when projected on the c face, will reveal a hexagonal framework.

$H_2(K, NH_4)(Al, Fe)(PO_4)_2$ (Group 3, Product E)

Only the potassium iron member of group 3 was obtained in crystals suitable for single-crystal x-ray study. The lattice constants were determined from a single setting. A rotation photograph, zero-, first- and second-layer line Weissenberg photographs, and composites of zero-layer with first-layer and with second-layer line photographs were taken about the c -axis. The primitive cell of three formula weights (Table 1) is somewhat unusual; if the crystal is centrosymmetric, at least one iron and one potassium must occupy centers of symmetry.

The dispersion formula given by Haseman *et al.* (1951) is reversed.

Leucophosphite, $(K, NH_4)(Al, Fe)_2(PO_4)_2(OH) \cdot 2H_2O$ (Group 4, Products I and J)

Powder diffraction data on a naturally occurring potassium iron phosphate, leucophosphite, from Bambuta, Liberia, showed it to be identical with one of the members of group 4 (Axelrod *et al.*, 1952). The lattice constants, space group and optical properties of a leucophosphite from Minas Gerais, Brazil, were reported by Lindberg (1957). The extinction angles ($z \wedge c$) given by Lindberg and by Haseman (1951) are consistent, since Lindberg refers to the b -centered cell and Haseman to obtuse β in the primitive cell. The dispersion formula given by Haseman *et al.* (1951) is reversed.

The potassium iron and ammonium aluminum isomorphs were used in this study. The observed reflections, hkl present in all orders, $h0l$ present only when $h+l=2n$, and $0k0$ present only when $k=2n$, agree

with those reported by Lindberg. The most probable space group for both compounds is $C_{2h}^5-P2_1/n$. The lattice constants for the natural and the synthetic potassium iron materials agree within the expected experimental errors.

$H_8(K, NH_4)(Al, Fe)_3(PO_4)_6 \cdot 6H_2O$ (Group 5, Product K)

The synthetic compounds of group 5 crystallize in the hexagonal system as thin plates or short rods. They are formed readily in acid solutions containing iron and phosphate. The ammonium or potassium content is variable; they apparently can be formed with few, perhaps even none, of these ions in the lattice. Only the ammonium iron compound was obtained in crystals suitable for Weissenberg study. The respective powder diffraction patterns indicate that the potassium iron compound has essentially the same unit-cell dimensions. The lattice parameters listed in Table 1 for the ammonium aluminum compound were derived from an indexing of the first 27 lines of the powder diffraction pattern.

The observed reflections in the Weissenberg patterns, $hk\bar{l}$ and $h\bar{h}0l$ present in all orders, $hh2\bar{h}l$ present only when $l=2n$, correspond with the possible space groups $D_{6h}^4-P6_3/mmc$, $C_{6v}^4-P6_3mc$ and $D_{3h}^4-P\bar{6}2c$. The most probable space group could not be decided from etch experiments and morphology. Once the correct space group is established, a determination of the structure should be straightforward, in view of the many restrictions imposed by the symmetry elements on the positions of the atoms.

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