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Crystal structure of synthetic $(\text{NH}_4)_8\text{Fe}^{3+}(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$

PAUL B. MOORE AND TAKAHARU ARAKI

Department of the Geophysical Sciences, The University of Chicago
Chicago, Illinois 60637

Abstract

Product K, $(\text{NH}_4)_8\text{Fe}^{3+}(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$, is based on corner-linking octahedra and tetrahedra and is structurally related to coquimbite, paracoquimbite, and the synthetic $\text{Fe}_2(\text{SO}_4)_3$ dimorphs. It is trigonal, $a_1 = 9.151(2)$, $c = 16.862(4)\text{Å}$, $Z = 2$, space group $P31c$; usually merohedrally twinned leading to $6/m$ $2/m$ $2/m$ intensity distributions.

$R = 0.042$ for 1200 non-equivalent reflections. The general formula can be written $(\text{NH}_4)\text{Fe}^{3+}[\text{PO}_2(\text{OH})_{2/3}\text{O}_{1/3}]_3[\text{PO}_2(\text{OH})_2]_2(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$. Average bond distances are $\text{Fe}(1)-(\text{O}, \text{H}_2\text{O})$ 2.010 Å, $\text{Fe}(2)-\text{O}$ 1.983 Å, $\text{Fe}(3)-\text{O}$ 2.005 Å, $\text{P}(1)-(\text{O}, \text{OH})$ 1.538 Å, $\text{P}(2)-(\text{O}, \text{OH})$ 1.545 Å, $\text{NH}_4^+-(\text{OH}, \text{H}_2\text{O})$ 3.06 Å; the ammonium cation is in distorted octahedral coordination. Two of the three independent $\text{Fe}-\text{O}$ octahedra (M) on three-fold rotors and all of the phosphate tetrahedra (T) link at ϕ (linking oxygen) to form a framework structure of stoichiometry $MT_3\phi_6$.

Introduction

We have been much interested in anisodesmic oxysalts of ferric iron and aluminum and extended our study to phases which arise under more acid conditions. Particularly in the phosphates, considerable uncertainty exists in the explicit expression of the structure formula, since the presence of protons suggests the possibility of "acid phosphate" anions. One problem concerns the distribution of these protons and the consequent effect on structure geometry. The compound whose structure we report is called Product K and was studied, along with four other related compounds, by Smith and Brown (1959). One of these compounds is taranakite, $\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_6 \cdot 18\text{H}_2\text{O}$, whose complex structure is unknown but may be related to Product K, which has not as yet been found as a natural phase. We hoped that knowledge of Product K's structure would assist in eventual deciphering of taranakite, which so far has not been found in suitable crystals. Our results provide structural relationships between acid phosphates and other anisodesmic oxysalts, particularly sulfates. In addition, the structure suggests a family of corner-sharing framework structures based on octahedral and tetrahedral corner-sharing linkages, which may represent a new class of zeolitic structures.

Experimental section

Single crystals of Product K were kindly provided by Mr. James R. Lehr of the Tennessee Valley Authority. Smith and Brown (1959) reported $2[\text{H}_8(\text{NH}_4)\text{Fe}^{3+}(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}]$, space group $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$, specific gravity (pycnometric) 2.36, computed density 2.36 g cm^{-3} , $a = 9.14$, $c = 16.88\text{Å}$. In addition they reported synthesis of potassium and aluminum analogues, and found that the structure can tolerate a range of alkali contents and possibly can form without these cations, an observation which added interest to its structure.

The crystal selected for our structure analysis measured $0.10\text{mm} (\parallel a_1) \times 0.12\text{mm} (\parallel a_2) \times 0.20\text{mm} (\parallel c)$. Data were collected by ω -scan on a Picker automated diffractometer (graphite monochromator, $\text{MoK}\alpha$ radiation, $\lambda = 0.70926\text{Å}$) to $2\theta = 60.0^\circ$ with scan speed 2° min^{-1} and base scan width of 2° . Background counting times were 20 sec on each side of the peak. Refined cell data from the orientation matrix are $a = 9.151(2)$, $c = 16.862(4)\text{Å}$, in good agreement with the earlier study. A total of 2545 reflections was collected in the reciprocal space sector ($\bar{h}kl$), including $h = 12$ to 0, $k = 0$ to 12 and $l = 0$ to 23. No absorption correction was applied because of favorable crystal shape and low linear absorption coefficient of $u =$

STRUCTURE FACTOR TABLE FOR

8/24/77 FE (NH₄) ACID PHOSPHATE

ONE SHEET OF TABLE COMPOSED OF

COLUMNS ON PAGE (PART)

4
4
4
2

H	K	L	FO	FC	M	K	L	FO	FC	I	K	L	FO	FC	M	K	L	FO	FC	I	K	L	FO	FC	M	K	L	FO	FC	
0	0	0	2	73.4	83.4	0	7	3	31.1	30.1	1	15	50.6	49.0	1	6	19	19.2	17	9	0	0	0	0	0	0	0	0	0	0
0	0	0	4	69.0	83.1	0	7	4	52.1	53.0	1	14	68.0	67.7	1	7	-17	16.2	17	0	0	0	0	0	0	0	0	0	0	
0	0	0	6	84.1	81.9	0	7	5	11.5	13.9	1	13	60.0	58.7	1	7	-16	24.6	22.2	22	2	0	0	0	0	0	0	0	0	0
0	0	0	8	156.0	157.4	0	7	6	26.7	26.8	1	12	41.0	40.7	1	7	-15	16.5	13.4	13	4	0	0	0	0	0	0	0	0	0
0	0	0	10	37.8	37.6	0	7	7	50.3	50.0	1	11	52.7	52.1	1	7	-14	30.4	31.8	31	8	0	0	0	0	0	0	0	0	0
0	0	0	12	111.5	114.2	0	7	8	11.1	10.6	1	10	3.4	5.0	1	7	-13	21.4	19.8	19	8	0	0	0	0	0	0	0	0	0
0	0	0	14	197.8	196.6	0	7	9	10.7	9.9	1	9	56.2	51.9	1	7	-12	28.1	26.5	26	5	0	0	0	0	0	0	0	0	0
0	0	0	16	62.2	65.2	0	7	10	5.0	2.9	1	8	47.6	44.5	1	7	-11	19.1	17.2	17	2	0	0	0	0	0	0	0	0	0
0	0	0	18	24.7	21.5	0	7	11	31.7	31.7	1	7	60.0	57.6	1	7	-10	44.0	43.9	43	9	0	0	0	0	0	0	0	0	0
0	0	0	20	33.3	34.0	0	7	12	29.1	27.1	1	7	59.5	61.3	1	7	-9	21.6	19.7	19	7	0	0	0	0	0	0	0	0	0
0	0	0	22	63.5	62.3	0	7	13	23.7	23.7	1	7	59.5	61.3	1	7	-8	20.1	19.7	19	7	0	0	0	0	0	0	0	0	0
0	0	0	24	40.6	42.0	0	7	14	14.7	14.7	1	7	46.7	47.6	1	7	-7	11.1	10.1	10	1	0	0	0	0	0	0	0	0	0
0	0	0	26	99.2	103.7	0	7	15	15.7	15.3	1	7	96.0	96.0	1	7	-6	25.6	26.0	26	0	0	0	0	0	0	0	0	0	0
0	0	0	28	90.0	87.7	0	7	16	14.6	14.8	1	7	73.7	76.2	1	7	-5	25.8	26.2	26	2	0	0	0	0	0	0	0	0	0
0	0	0	30	37.4	34.8	0	7	17	19.3	18.2	1	7	31.6	31.6	1	7	-4	43.0	42.9	42	9	0	0	0	0	0	0	0	0	0
0	0	0	32	64.2	65.0	0	7	18	28.1	29.4	1	7	26.4	26.4	1	7	-3	23.4	24.9	24	9	0	0	0	0	0	0	0	0	0
0	0	0	34	5.6	11.0	0	7	19	11.0	11.1	1	7	60.6	60.6	1	7	-2	38.9	37.9	37	9	0	0	0	0	0	0	0	0	0
0	0	0	36	4.1	4.1	0	7	20	37.7	38.1	1	7	28.0	28.0	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	38	12.1	12.1	0	7	21	28.3	29.4	1	7	25.6	24.5	1	7	-4	43.0	42.9	42	9	0	0	0	0	0	0	0	0	0
0	0	0	40	2.3	2.3	0	7	22	30.3	31.3	1	7	29.7	29.7	1	7	-3	23.4	24.9	24	9	0	0	0	0	0	0	0	0	0
0	0	0	42	30.7	30.7	0	7	23	21.1	21.1	1	7	23.1	22.9	1	7	-2	38.9	37.9	37	9	0	0	0	0	0	0	0	0	0
0	0	0	44	19.1	14.8	0	7	24	14.8	14.8	1	7	19.1	19.1	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	46	49.0	31.3	0	7	25	31.3	31.3	1	7	18.0	17.8	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	48	64.3	50.9	0	7	26	27.2	27.2	1	7	15.9	15.9	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	50	65.9	64.3	0	7	27	27.2	27.2	1	7	12.6	12.6	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	52	33.7	33.7	0	7	28	34.3	34.3	1	7	10.4	10.4	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	54	61.4	61.4	0	7	29	36.0	37.6	1	7	9.0	9.0	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	56	16.9	16.9	0	7	30	37.3	37.9	1	7	7.6	8.8	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	58	27.6	27.6	0	7	31	21.1	21.1	1	7	6.4	6.4	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	60	13.9	13.9	0	7	32	21.1	21.1	1	7	5.2	5.2	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	62	10.7	10.7	0	7	33	21.1	21.1	1	7	4.0	4.0	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	64	17.4	17.4	0	7	34	21.1	21.1	1	7	2.8	2.8	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	66	14.2	14.2	0	7	35	21.1	21.1	1	7	1.6	1.6	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	68	16.0	16.0	0	7	36	21.1	21.1	1	7	0.4	0.4	1	7	-1	23.1	23.0	23	0	0	0	0	0	0	0	0	0	0
0	0	0	70	14.2	14.2	0	7	37	21.1	21.1	1	7	-0.2	-0.2	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	72	12.5	12.5	0	7	38	21.1	21.1	1	7	-1.4	-1.4	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	74	19.7	19.7	0	7	39	21.1	21.1	1	7	-2.2	-2.2	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	76	19.7	19.7	0	7	40	21.1	21.1	1	7	-3.0	-3.0	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	78	19.7	19.7	0	7	41	21.1	21.1	1	7	-3.8	-3.8	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	80	19.7	19.7	0	7	42	21.1	21.1	1	7	-4.6	-4.6	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	82	19.7	19.7	0	7	43	21.1	21.1	1	7	-5.4	-5.4	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	84	19.7	19.7	0	7	44	21.1	21.1	1	7	-6.2	-6.2	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	86	19.7	19.7	0	7	45	21.1	21.1	1	7	-7.0	-7.0	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	88	19.7	19.7	0	7	46	21.1	21.1	1	7	-7.8	-7.8	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	90	19.7	19.7	0	7	47	21.1	21.1	1	7	-8.6	-8.6	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	92	19.7	19.7	0	7	48	21.1	21.1	1	7	-9.4	-9.4	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	94	19.7	19.7	0	7	49	21.1	21.1	1	7	-10.2	-10.2	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	96	19.7	19.7	0	7	50	21.1	21.1	1	7	-11.0	-11.0	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	98	19.7	19.7	0	7	51	21.1	21.1	1	7	-11.8	-11.8	1	7	0	47.1	47.1	47	1	0	0	0	0	0	0	0	0	0
0	0	0	100	19.7	19.7	0	7	52	21.1	21.1	1	7	-12.6	-12.6	1	7	0	47.1	47.1											

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	43.9	42.8	2	7	-6	33.8	34.5	39.9	39.4	0	23.9	25.7							
0	43.4	41.9	2	7	-5	13.0	12.1	33.0	32.8	1	20.1	20.5							
1	43.5	44.9	2	7	-4	30.5	29.2	29.3	30.0	2	31.1	31.1							
2	60.2	59.7	2	7	-3	35.2	33.6	20.0	17.3	3	40.7	42.0							
3	63.4	64.4	2	7	-2	13.2	13.0	30.4	32.3	4	38.7	39.4							
4	46.9	48.5	2	7	-1	27.8	26.5	5.3	6.5	5	34.2	34.6							
5	44.5	45.5	2	7	0	6.8	5.5	29.4	26.9	6	28.7	28.5							
6	53.3	51.3	2	7	1	26.8	24.7	6.6	5.0	7	50.2	46.5							
7	35.8	36.2	2	7	1	15.6	14.1	55.2	52.9	8	31.0	29.5							
8	63.2	62.3	2	7	0	30.0	31.0	3.5	7.9	9	17.4	17.1							
9	31.5	32.3	2	7	4	32.0	31.1	10	20.2	10	16.5	15.6							
10	53.4	53.6	2	7	5	9.5	11.5	11	20.8	19.3	11	37.0	38.7						
11	33.0	34.6	2	7	6	33.1	36.4	12	18.2	19.5	12	23.7	24.5						
12	21.0	21.8	2	7	7	43.2	42.1	13	19.3	20.7	13	31.0	30.1						
13	10.5	13.0	2	7	8	35.5	36.5	14	12	18.2	15	29.8	30.0						
14	40.9	39.7	2	7	9	14.0	15.3	14	19.5	20.7	14	31.0	30.1						
15	34.7	35.0	2	7	10	8.6	7.8	15	10.2	11.0	15	29.8	30.0						
16	18.9	20.7	2	7	11	24.8	24.0	16	10.0	11.0	16	19.7	17.1						
17	36.7	37.6	2	7	12	18.0	17.0	17	19.3	19.1	17	9.4	9.5						
18	27.9	29.0	2	7	13	22.3	21.2	18	19.1	18.1	18	7.4	7.5						
19	21.8	25.2	2	7	14	16.3	14.6	19	16.2	15.3	19	10.9	10.9						
20	20.5	20.3	2	7	15	15.0	14.3	20	14.6	16.3	20	21.7	21.6						
21	16.1	16.8	2	7	16	9.9	9.9	21	16.0	15.3	21	33.5	33.3						
22	9.9	8.2	2	7	17	13	12	22	19.1	18.1	22	9.5	9.5						
23	-1.9	16.5	16.1	2	7	-12	20.8	18.8	19	16.2	15.3	-12	9.0	9.3					
24	-1.9	51.1	48.7	2	7	-11	6.7	6.7	23	16.2	15.3	11	11.4	11.4					
25	-1.9	16.6	18.2	2	7	-10	3.3	3.3	24	14.6	15.3	10	19.2	17.8					
26	-1.9	28.4	28.7	2	7	-9	2.2	2.2	25	12.0	12.0	9	8.3	8.3					
27	-1.9	38.1	38.6	2	7	-8	1.3	1.3	26	10.4	12.0	8	7.3	7.3					
28	-1.9	21.0	21.8	2	7	-7	1.3	1.3	27	8.0	9.0	7	11.4	11.4					
29	-1.9	15.0	16.7	2	7	-6	1.3	1.3	28	6.0	7.0	6	35.0	35.6					
30	-1.9	33.0	31.5	2	7	-5	1.3	1.3	29	4.0	5.0	5	12.1	12.7					
31	-1.9	37.7	37.5	2	7	-4	1.3	1.3	30	2.0	3.0	4	4.0	4.9					
32	-1.9	27.9	26.3	2	7	-3	1.3	1.3	31	0.0	1.0	3	20.9	27.4					
33	-1.9	27.0	27.0	2	7	-2	1.3	1.3	32	0.0	1.0	2	35.0	25.1					
34	-1.9	15.6	14.7	2	7	-1	1.3	1.3	33	0.0	1.0	1	12.1	20.4					
35	-1.9	11.2	8.4	2	7	0	1.3	1.3	34	0.0	1.0	0	19.6	19.6					
36	-1.9	17.8	22.4	2	7	-1	1.3	1.3	35	0.0	1.0	-1	11.5	11.5					
37	-1.9	22.6	23.6	2	7	0	1.3	1.3	36	0.0	1.0	1	11.5	11.5					
38	-1.9	27.7	27.0	2	7	0	1.3	1.3	37	0.0	1.0	0	28.7	27.7					
39	-1.9	15.6	14.7	2	7	0	1.3	1.3	38	0.0	1.0	-1	25.3	25.1					
40	-1.9	11.2	8.4	2	7	0	1.3	1.3	39	0.0	1.0	0	35.0	35.6					
41	-1.9	17.1	17.0	2	7	0	1.3	1.3	40	0.0	1.0	-1	4.0	4.9					
42	-1.9	66.5	65.5	2	7	0	1.3	1.3	41	0.0	1.0	0	4.0	4.9					
43	-1.9	31.7	30.9	2	7	0	1.3	1.3	42	0.0	1.0	-1	12.0	12.0					
44	-1.9	55.0	55.3	2	7	0	1.3	1.3	43	0.0	1.0	0	11.6	11.6					
45	-1.9	66.7	64.9	2	7	0	1.3	1.3	44	0.0	1.0	-1	14.0	14.0					
46	-1.9	17.0	17.1	2	7	0	1.3	1.3	45	0.0	1.0	0	12.0	12.0					
47	-1.9	66.2	64.0	2	7	0	1.3	1.3	46	0.0	1.0	-1	11.6	11.6					
48	-1.9	35.1	31.1	2	7	0	1.3	1.3	47	0.0	1.0	0	12.0	12.0					

22-9 22-8
28-9 27-8
34-3 33-6
24-9 23-0
18-6 16-3
17-7 19-0
11-1 12-9
-11 23-7
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-9 21-1
-5 20-2
-6 19-4
-11 18-3
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