

Rietveld refinement of whitlockite-related  $K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$ 

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Key indicators: powder X-ray study;  $T = 293$  K; mean  $\sigma(P-O) = 0.024$  Å; disorder in main residue;  $R$  factor = 8.711;  $wR$  factor = 11.243; data-to-parameter ratio = 5.4.

The title compound,  $K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$  (potassium decacalcium iron heptaphosphate), belongs to the whitlockite family. The structure is built up from several types of metal–oxygen polyhedra: two  $[CaO_8]$ , one  $[CaO_7]$  and one  $[(Ca/Fe)O_6]$  polyhedron with a mixed Ca/Fe occupancy in a 0.8:0.2 ratio, as well as three tetrahedral  $[PO_4]$  units. Of the 18 sites in the asymmetric unit, the site with the mixed Ca/Fe occupation, the K site, one P and one O site are on special positions  $6a$  with 3 symmetry, whereas all other sites are on general positions  $18b$ . The linkage of metal–oxygen polyhedra and  $[PO_4]$  tetrahedra *via* edges and corners results in formation of a three-dimensional framework with composition  $[Ca_{9.8}Fe_{0.2}(PO_4)_7]^{0.8-}$ . The remaining K atoms (site-occupation factor = 0.8) are located in large closed cavities and are nine-coordinated by oxygen.

## Related literature

For the structure of the mineral whitlockite with idealized composition  $Ca_3(PO_4)_2$  ( $\beta$ -polymorph), see: Calvo & Gopal (1975); Yashima *et al.* (2003). For  $KCa_{10}(PO_4)_7$ , see: Sandström & Boström (2006). For powder diffraction investigations and Rietveld refinements of other phosphate-based whitlockites, see: Morozov *et al.* (2000) for  $M^I Ca_{10}(PO_4)_7$  ( $M^I = Li, Na, K$ ); Lazoryak *et al.* (1996) for  $Ca_9Fe(PO_4)_7$ ; Morozov *et al.* (2002) for  $Ca_9In(PO_4)_7$ ; Strunenkov *et al.* (1997) for  $Na_{1.5}Ca_9Fe_{0.5}(PO_4)_7$ . For the profile function used in the Rietveld refinement, see: Thompson *et al.* (1987).

## Experimental

## Crystal data

$K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$   
 $M_r = 1100.02$   
Trigonal,  $R3c$

$a = 10.44282$  (1) Å  
 $c = 37.29443$  (3) Å  
 $V = 3522.17$  (1) Å<sup>3</sup>

$Z = 6$   
Cu  $K\alpha$  radiation,  $\lambda = 1.540598$  Å

$T = 293$  K  
Flat sheet,  $25 \times 25$  mm

## Data collection

Shimadzu LabX XRD-6000 diffractometer  
Specimen mounting: glass container  
Data collection mode: reflection

Scan method: step  
 $2\theta_{\min} = 8.92^\circ$ ,  $2\theta_{\max} = 99.92^\circ$ ,  
increment in  $2\theta = 0.02^\circ$

## Refinement

$R_p = 8.711$   
 $R_{wp} = 11.243$   
 $R_{exp} = 4.919$   
 $R_{Bragg} = 3.849$

$R(F) = 2.48$   
4551 data points with 839 reflections  
131 parameters  
4 restraints

Table 1

Selected bond lengths (Å).

Ca1—O11 <sup>i</sup>	2.519 (10)	Ca3—O31 <sup>vii</sup>	2.47 (4)
Ca1—O21 <sup>ii</sup>	2.702 (13)	Ca3—O33 <sup>vii</sup>	2.78 (3)
Ca1—O22	2.51 (3)	Ca3—O34	2.60 (3)
Ca1—O23 <sup>iii</sup>	2.40 (2)	Ca4—O24	2.30 (3)
Ca1—O32	2.579 (17)	Ca4—O31	2.23 (4)
Ca1—O32 <sup>iii</sup>	2.57 (2)	Fe4—O24	2.30 (3)
Ca1—O33 <sup>iii</sup>	2.59 (3)	Fe4—O31	2.23 (4)
Ca1—O34	2.48 (3)	K1—O12	2.90 (3)
Ca2—O12 <sup>ii</sup>	2.474 (16)	K1—O21	2.508 (19)
Ca2—O23 <sup>iv</sup>	2.63 (3)	K1—O22	3.25 (3)
Ca2—O24 <sup>iv</sup>	2.444 (19)	P1—O11	1.51 (4)
Ca2—O24 <sup>v</sup>	2.48 (3)	P1—O12	1.62 (2)
Ca2—O32 <sup>v</sup>	2.41 (2)	P2—O21	1.49 (2)
Ca2—O33 <sup>iii</sup>	2.21 (3)	P2—O22	1.56 (2)
Ca2—O34	2.36 (3)	P2—O23	1.53 (2)
Ca3—O12	2.295 (15)	P2—O24	1.486 (17)
Ca3—O21	2.48 (2)	P3—O31	1.62 (3)
Ca3—O22 <sup>vi</sup>	2.49 (3)	P3—O32	1.53 (3)
Ca3—O23 <sup>iv</sup>	2.30 (3)	P3—O33	1.57 (3)
Ca3—O31	2.38 (3)	P3—O34	1.63 (2)

Symmetry codes: (i)  $-x + y + \frac{2}{3}, y + \frac{1}{3}, z - \frac{1}{6}$ ; (ii)  $-x + y, -x, z$ ; (iii)  $-y + 1, x - y, z$ ; (iv)  $x + \frac{1}{3}, x - y + \frac{2}{3}, z + \frac{1}{6}$ ; (v)  $-x + y + \frac{1}{3}, y - \frac{1}{3}, z + \frac{1}{6}$ ; (vi)  $-y + \frac{1}{3}, -x + \frac{2}{3}, z + \frac{1}{6}$ ; (vii)  $-x + y, -x + 1, z$ .

Data collection: *PCXRD* (Shimadzu, 2006); cell refinement: *DICVOL 2004* (Boultif & Louër, 2004); data reduction: *FULLPROF* (Rodriguez-Carvajal, 2006); program(s) used to solve structure: *FULLPROF*; program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2324).

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## supporting information

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**Rietveld refinement of whitlockite-related  $\text{K}_{0.8}\text{Ca}_{9.8}\text{Fe}_{0.2}(\text{PO}_4)_7$** 

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**S1. Comment**

In the compound  $\text{K}_{0.8}\text{Ca}_{9.8}\text{Fe}_{0.2}(\text{PO}_4)_7$  (I), atoms Ca4/Fe4, K1, P1 and O11 are in special positions  $6a$  that lie on a 3-fold rotation axis, whereas all other atoms are located in general positions  $18b$  (Fig. 1).

Compound (I) might be represented as a result of an aliovalent substitution of calcium atoms in  $\beta\text{-Ca}_3(\text{PO}_4)_2$  (Calvo *et al.*, 1975; Yashima *et al.*, 2003) by a pair of K and Fe atoms.

$[\text{CaO}_x]$  polyhedra (two types of  $[\text{CaO}_8]$ , one of  $[\text{CaO}_7]$  and one  $[(\text{Ca}/\text{Fe})\text{O}_6]$  with mixed Fe/Ca occupancy) and three different  $[\text{PO}_4]$  tetrahedra are linked via edges and corners to build a three-dimensional framework with composition  $[\text{Ca}_{9.8}\text{Fe}_{0.2}(\text{PO}_4)_7]^{0.8-}$  (Fig. 2). The  $\text{K}^+$  cations are located in large closed cavities inside the framework (K1 occupancy is equal to 0.8).

For (I), Ca—O distances of  $[\text{CaO}_8]$ - and  $[\text{CaO}_7]$ -polyhedra (2.295 (15)–2.78 (3) Å) are close to these in previously reported isotypic compounds  $s\text{-Ca}_9\text{Fe}(\text{PO}_4)_7$  (2.29 (3)–2.73 (3) Å),  $o\text{-Ca}_9\text{Fe}(\text{PO}_4)_7$  (2.29 (3)–2.70 (4) Å) (Lazoryak *et al.*, 1996) and  $\text{KCa}_{10}(\text{PO}_4)_7$  (2.329 (3)–2.76 (2) Å) (Sandström & Boström, 2006). The distances Ca/Fe—O (2.23 (4)–2.29 (3) Å) within the  $[(\text{Ca}/\text{Fe})\text{O}_6]$  polyhedron are close to these of the  $[\text{CaO}_6]$  polyhedron in  $\text{KCa}_{10}(\text{PO}_4)_7$  (2.239 (4)–2.267 (4) Å), while they significantly differ from  $d(\text{Fe—O}) = 1.95$  (3)–2.17 (3) Å in  $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$ .

Potassium atoms are nine-coordinated (three triples of K—O distances in the range of 2.508 (19)–3.24 (3) Å) (Fig. 3), while in  $\text{KCa}_{10}(\text{PO}_4)_7$  the K—O contacts vary in the range of 2.641 (3)–3.25 (4) Å.

In conclusion, compound (I) can be considered as a solid solution within the  $\text{KCa}_{10}(\text{PO}_4)_7 / \text{Ca}_9\text{Fe}(\text{PO}_4)_7$  double system.

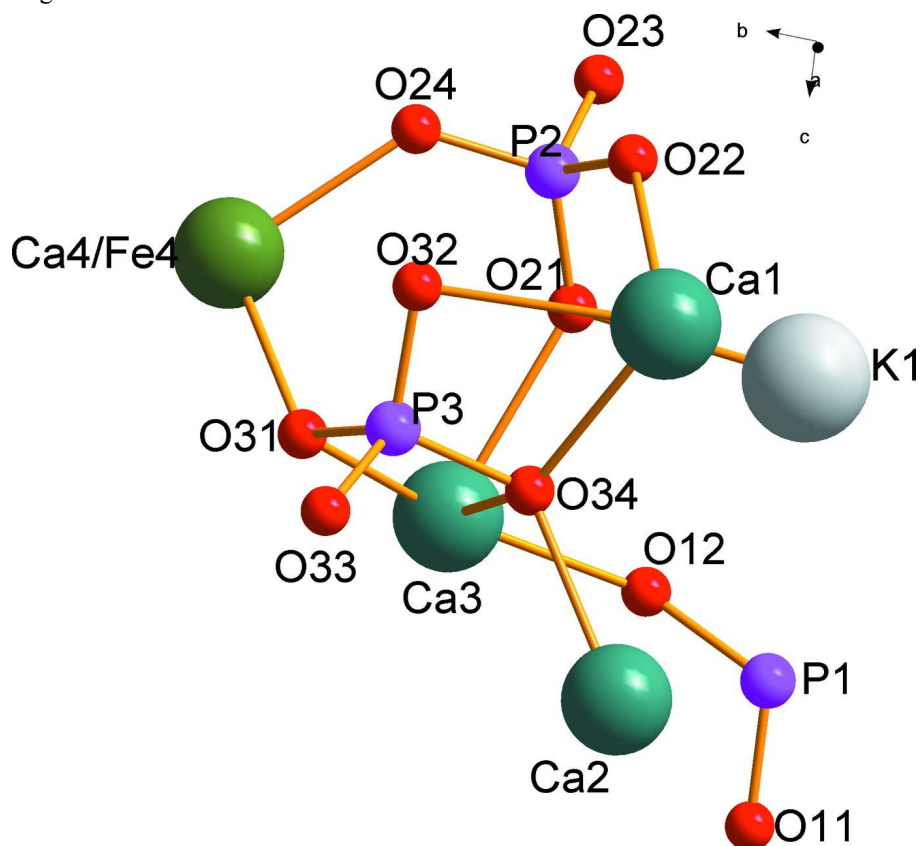
**S2. Experimental**

The title compound was prepared by solid state reaction from a mixture of  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in the molar ratio K/Ca/Fe/P = 0.8:9.8:0.2:7.0. The reagents were finely ground in an agate mortar and then placed in a porcelain crucible. The thermal treatment was carried out in three steps. The first included preheating to 873 K to decompose the ammonium salt and carbonates. After that, the mixture was heated at 1273 K for 12 h, cooled to room temperature, reground, and held at 1373 K for 6 h. The resulting product was a pale pink powder.

**S3. Refinement**

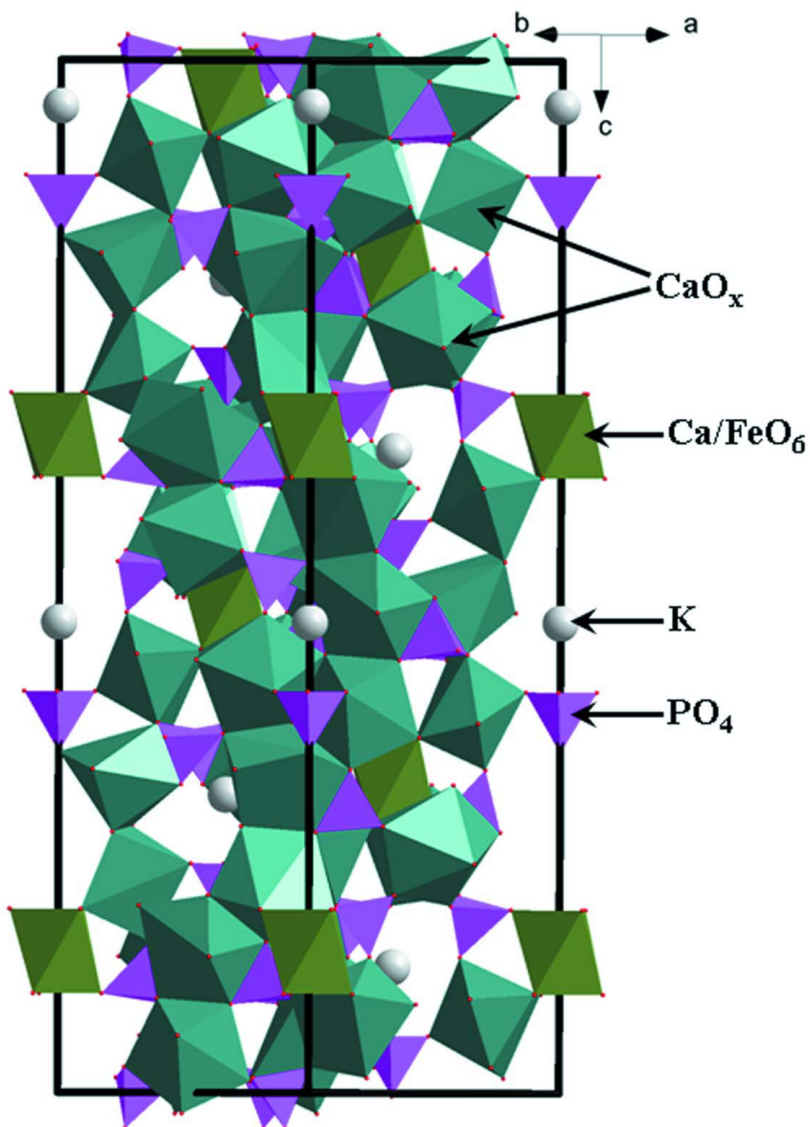
The powder pattern was indexed in rhombohedral cell (hexagonal setting) by *Dicvol 2004* (Boultif & Louër, 2004). The structure of  $\text{KCa}_{10}(\text{PO}_4)_7$  (Sandström & Boström, 2006) was selected as a starting model for Rietveld refinement. Profile matching refinement was performed firstly. Then scaling factor and background were added to the refined parameters. The background was approximated using linear interpolation between a set of background points with refineable heights. A modified pseudo-Voigt function (Thompson *et al.*, 1987) was used for the profile refinement. As it was determined previously, only one position of calcium is suitable for heterovalent substitution by a three-valent  $3d$ -metal. It is the

octahedrally coordinated Ca4 site. Thus the iron site was placed into the Ca4 position. The occupancy of iron was fixed at 0.2 while the remaining calcium occupancy was set to 0.8. The potassium occupancy was set to 0.8 due to electroneutrality of the compound. The atomic coordinates and  $B_{\text{iso}}$  of Ca and Fe were constrained to be equal. ADPs of all P atoms were constrained to be equal as well as the ADPs of all O atoms. The value of  $B_{\text{iso}}$  for Ca4 was restrained in the range of 0.17-0.3. The value of  $B_{\text{iso}}$  for O11 was also restrained in the range of 0.2-0.3. Two distance restraints for P2—O21 and P2—O23 bonds were applied. Experimental, calculated and difference patterns after the final refinement cycle are shown in Fig. 4.

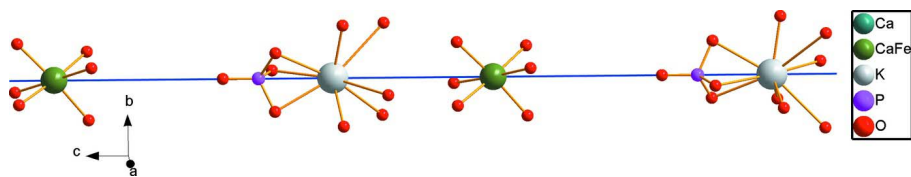


**Figure 1**

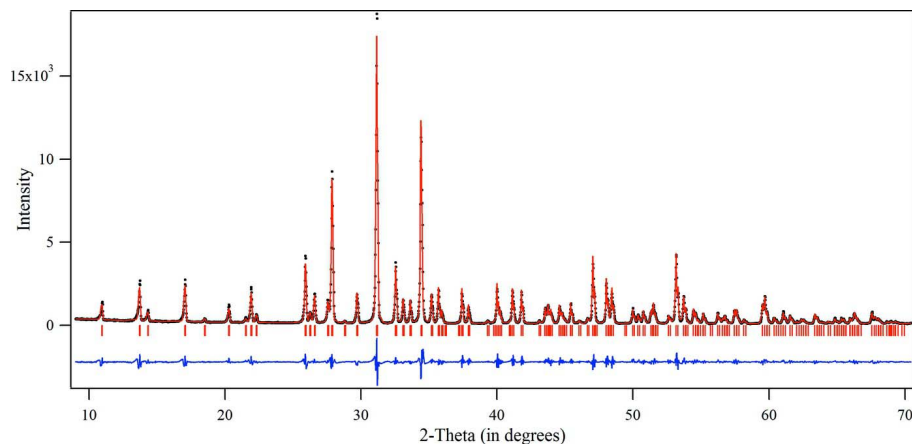
A view of the unit cell content of compound (I).



**Figure 2**  
Connectivity of the metal-oxygen polyhedra and  $\text{PO}_4$  groups in (I).



**Figure 3**  
Coordination environment of the atoms in  $6a$  position.



**Figure 4**

Rietveld refinement of  $\text{K}_{0.8}\text{Ca}_{9.8}\text{Fe}_{0.2}(\text{PO}_4)_7$ . Experimental (dots), calculated (red curve) and difference (blue curve) data for  $2\theta$  range  $9\text{--}72^\circ$ .

### potassium decacalcium iron heptaphosphate

#### Crystal data

$\text{K}_{0.8}\text{Ca}_{9.8}\text{Fe}_{0.2}(\text{PO}_4)_7$

$M_r = 1100.02$

Trigonal,  $R3c$

Hall symbol:  $R\ 3\ -2''c$

$a = 10.44282(1)\ \text{\AA}$

$c = 37.29443(3)\ \text{\AA}$

$V = 3522.17(1)\ \text{\AA}^3$

$Z = 6$

$D_x = 3.112\ \text{Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.540598\ \text{\AA}$

$T = 293\ \text{K}$

Particle morphology: isometric

light pink

flat sheet,  $25 \times 25\ \text{mm}$

Specimen preparation: Prepared at 293 K and 101.3 kPa

#### Data collection

Shimadzu LabX XRD-6000

diffractometer

Radiation source: X-ray tube, X-ray

Graphite monochromator

Specimen mounting: glass container

Data collection mode: reflection

Scan method: step

$2\theta_{\min} = 8.915^\circ$ ,  $2\theta_{\max} = 99.915^\circ$ ,  $2\theta_{\text{step}} = 0.020^\circ$

#### Refinement

$R_p = 8.711$

$R_{\text{wp}} = 11.243$

$R_{\text{exp}} = 4.919$

$R_{\text{Bragg}} = 3.849$

$R(F) = 2.48$

4551 data points

Excluded region(s): undef

Profile function: Thompson–Cox–Hastings

pseudo-Voigt \* Axial divergence asymmetry

131 parameters

4 restraints

4 constraints

Standard least squares refinement

$(\Delta\sigma)_{\max} = 0.001$

Background function: Linear Interpolation

between a set background points with refinable heights

Preferred orientation correction: Modified

March's Function

#### Special details

**Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ca1	0.3986 (5)	0.1868 (7)	0.0212 (4)	0.0022 (18)*	
Ca2	0.3922 (6)	0.1887 (10)	0.1265 (4)	0.0022 (16)*	
Ca3	0.1776 (11)	0.3817 (6)	0.0949 (5)	0.003 (2)*	
Ca4	0.33333	0.66667	0.0288 (5)	0.002 (2)*	0.80000
Fe4	0.33333	0.66667	0.0288 (5)	0.002 (2)*	0.20000
K1	0.00000	0.00000	0.0447 (5)	0.004 (4)*	0.80000
P1	0.00000	0.00000	0.1293 (5)	0.0031 (11)*	
P2	0.1351 (9)	0.3124 (6)	-0.0032 (4)	0.0031 (11)*	
P3	0.4897 (11)	0.4749 (11)	0.0609 (5)	0.0031 (11)*	
O11	0.00000	0.00000	0.1699 (8)	0.0025 (11)*	
O12	0.0071 (19)	0.1449 (14)	0.1115 (7)	0.0025 (11)*	
O21	0.0912 (15)	0.2697 (15)	0.0349 (4)	0.0025 (11)*	
O22	0.222 (2)	0.233 (2)	-0.0145 (6)	0.0025 (11)*	
O23	-0.0066 (16)	0.265 (2)	-0.0248 (5)	0.0025 (11)*	
O24	0.229 (3)	0.4728 (17)	-0.0110 (6)	0.0025 (11)*	
O31	0.408 (3)	0.567 (3)	0.0709 (7)	0.0025 (11)*	
O32	0.5039 (17)	0.4689 (16)	0.0203 (5)	0.0025 (11)*	
O33	0.6427 (19)	0.5475 (19)	0.0808 (6)	0.0025 (11)*	
O34	0.3720 (19)	0.3100 (19)	0.0752 (7)	0.0025 (11)*	

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
?	?	?	?	?	?	?

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ca1—O11 <sup>i</sup>	2.519 (10)	Ca4—O31 <sup>viii</sup>	2.23 (4)
Ca1—O21 <sup>ii</sup>	2.702 (13)	Fe4—O24 <sup>viii</sup>	2.30 (3)
Ca1—O22	2.51 (3)	Fe4—O24	2.30 (3)
Ca1—O23 <sup>ii</sup>	2.40 (2)	Fe4—O24 <sup>vii</sup>	2.30 (3)
Ca1—O32	2.579 (17)	Fe4—O31	2.23 (4)
Ca1—O32 <sup>iii</sup>	2.57 (2)	Fe4—O31 <sup>vii</sup>	2.23 (4)
Ca1—O33 <sup>iii</sup>	2.59 (3)	Fe4—O31 <sup>viii</sup>	2.23 (4)
Ca1—O34	2.48 (3)	K1—O12	2.90 (3)
Ca2—O12 <sup>ii</sup>	2.474 (16)	K1—O12 <sup>ii</sup>	2.90 (3)
Ca2—O23 <sup>iv</sup>	2.63 (3)	K1—O12 <sup>ix</sup>	2.90 (3)
Ca2—O24 <sup>iv</sup>	2.444 (19)	K1—O21	2.508 (19)
Ca2—O24 <sup>v</sup>	2.48 (3)	K1—O21 <sup>ii</sup>	2.508 (19)
Ca2—O32 <sup>v</sup>	2.41 (2)	K1—O21 <sup>ix</sup>	2.508 (19)
Ca2—O33 <sup>iii</sup>	2.21 (3)	K1—O22	3.25 (3)
Ca2—O34	2.36 (3)	K1—O22 <sup>ii</sup>	3.25 (3)
Ca3—O12	2.295 (15)	K1—O22 <sup>ix</sup>	3.25 (3)
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Ca3—O22 <sup>vi</sup>	2.49 (3)	P1—O12	1.62 (2)

Ca3—O23 <sup>iv</sup>	2.30 (3)	P1—O12 <sup>ix</sup>	1.62 (2)
Ca3—O31	2.38 (3)	P1—O12 <sup>ii</sup>	1.62 (2)
Ca3—O31 <sup>vii</sup>	2.47 (4)	P2—O21	1.49 (2)
Ca3—O33 <sup>vii</sup>	2.78 (3)	P2—O22	1.56 (2)
Ca3—O34	2.60 (3)	P2—O23	1.53 (2)
Ca4—O24 <sup>viii</sup>	2.30 (3)	P2—O24	1.486 (17)
Ca4—O24	2.30 (3)	P3—O31	1.62 (3)
Ca4—O24 <sup>vii</sup>	2.30 (3)	P3—O32	1.53 (3)
Ca4—O31	2.23 (4)	P3—O33	1.57 (3)
Ca4—O31 <sup>vii</sup>	2.23 (4)	P3—O34	1.63 (2)
O24—Fe4—O24 <sup>vii</sup>	82.8 (11)	O22—P2—O23	114.2 (13)
O24—Fe4—O31 <sup>vii</sup>	101.7 (10)	O22—P2—O24	108.3 (15)
O24 <sup>viii</sup> —Fe4—O31	101.6 (10)	O23—P2—O24	104.3 (15)
O31—Fe4—O31 <sup>viii</sup>	75.9 (12)	O31—P3—O32	110.2 (15)
O24 <sup>vii</sup> —Fe4—O31	175.2 (13)	O31—P3—O33	108.4 (15)
O31—Fe4—O31 <sup>vii</sup>	75.9 (14)	O31—P3—O34	102.1 (15)
O24 <sup>viii</sup> —Fe4—O31 <sup>viii</sup>	99.6 (11)	O32—P3—O33	113.1 (14)
O24 <sup>viii</sup> —Fe4—O24 <sup>vii</sup>	82.8 (11)	O32—P3—O34	108.6 (13)
O24 <sup>viii</sup> —Fe4—O31 <sup>vii</sup>	175.2 (12)	O33—P3—O34	113.8 (14)
O24 <sup>vii</sup> —Fe4—O31 <sup>viii</sup>	101.7 (11)	O12 <sup>ix</sup> —P1—O12 <sup>ii</sup>	104.3 (12)
O31 <sup>viii</sup> —Fe4—O31 <sup>vii</sup>	75.9 (13)	O11—P1—O12 <sup>ii</sup>	114.2 (11)
O24 <sup>vii</sup> —Fe4—O31 <sup>vii</sup>	99.6 (13)	O11—P1—O12	114.2 (11)
O24—Fe4—O31	99.6 (9)	O11—P1—O12 <sup>ix</sup>	114.2 (11)
O24—Fe4—O24 <sup>viii</sup>	82.8 (11)	O12—P1—O12 <sup>ix</sup>	104.4 (12)
O24—Fe4—O31 <sup>viii</sup>	175.2 (12)	O12—P1—O12 <sup>ii</sup>	104.4 (13)
O21—P2—O22	105.8 (12)	Fe4—O24—P2	128.4 (15)
O21—P2—O23	107.5 (11)	Fe4—O31—P3	121.8 (16)
O21—P2—O24	117.0 (13)		

Symmetry codes: (i)  $-x+y+2/3, y+1/3, z-1/6$ ; (ii)  $-x+y, -x, z$ ; (iii)  $-y+1, x-y, z$ ; (iv)  $x+1/3, x-y+2/3, z+1/6$ ; (v)  $-x+y+1/3, y-1/3, z+1/6$ ; (vi)  $-y+1/3, -x+2/3, z+1/6$ ; (vii)  $-x+y, -x+1, z$ ; (viii)  $-y+1, x-y+1, z$ ; (ix)  $-y, x-y, z$ .