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The calcioferrite group approved and kingsmountite redefined

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Abstract: The calcioferrite group has been formally approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposal 19-B). It comprises four minerals with *C*-centred monoclinic cells and general formula $Ca_4A^{2+}B^{3+}_4(PO_4)_6(OH)_4{\cdot}12H_2O$, where *A* and *B* = Mg and Fe for calcioferrite, Mg and Al for montgomeryite, Mn and Fe for zodacite and Mn and Al for fanfaniite, together with the triclinic mineral kingsmountite, $Ca_3Mn^{2+}Fe^{2+}Al_4(PO_4)_6(OH)_4{\cdot}12H_2O$. The minerals with *B* = Fe form the calcioferrite subgroup and those with *B* = Al form the montgomeryite subgroup.The triclinic member was recently approved as the mineral "aniyunwiyaite" (IMA2018-054). New measurements on the holotype specimen of kingsmountite, however, show that it has the same crystallographic and chemical properties as "aniyunwiyaite" and, consequently, "aniyunwiyaite" has been discredited as being kingsmountite. Kingsmountite is triclinic, $P\bar{1}$, with $a = 20.067(6)$ Å, $b = 13.197(4)$ Å, $c = 6.255(3)$ Å, $\alpha = 89.35(2)°$, $\beta = 91.21(2)°$, $\gamma = 112.20(2)°$, $V = 1533.4(10)$ Å^3 and $Z = 2$. The structure was solved and refined to $R_{obs} = 0.059$ for 4351 reflections with $I > 3\sigma(I)$. The crystal structure is a superstructure of the *C*-centred monoclinic montgomeryite structure, having a doubled a_m cell parameter. The superstructure results from ordering of octahedrally coordinated Mn in one of four independent 8-coordinated Ca sites, and ordering of *A* site cations, which in the $Ca_4AB_4(PO_4)_6(OH)_4{\cdot}12H_2O$ structures are statistically distributed over half-occupied sites.

Key-words: calcioferrite group; montgomeryite subgroup; kingsmountite; crystal structure; "aniyunwiyaite" discredited.

1. Introduction

The four phosphate minerals calcioferrite (Blum, 1858), montgomeryite (Larsen, 1940), kingsmountite (Dunn *et al.*, 1979) and zodacite (Dunn *et al.*, 1988) have been reported to have in common the same general formula, $Ca_4AB_4(PO_4)_6(OH)_4{\cdot}12H_2O$ and similar powder X-ray diffraction (PXRD) patterns, with *C*-centred monoclinic unit cells, $a \sim 10.1$, $b \sim 24.1$, $c \sim 6.3$ Å and $\beta \sim 91.2°$. *A* and *B* are divalent and trivalent cations, respectively, with A^{2+} and B^{3+} = Mg^{2+} and Fe^{3+} for calcioferrite, Mg^{2+} and Al^{3+} for montgomeryite, Fe^{2+} and Al^{3+} for kingsmountite, and Mn^{2+} and Fe^{3+} for zodacite. The minerals have been described in the literature as forming the calcioferrite group (Lafuente *et al.*, 2014) or the montgomeryite group (Dunn *et al.*, 1988), but neither the group nor the group name had previously been approved by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification (CNMNC). Following the recent approvals by the CNMNC of fanfaniite, $Ca_4MnAl_4(PO_4)_6(OH)_4{\cdot}12H_2O$ (Grey *et al.*, 2018), the Mn-analogue of montgomeryite, and the related mineral "aniyunwiyaite", $Ca_3Mn^{2+}Fe^{2+}Al_4(PO_4)_6(OH)_4{\cdot}12H_2O$ (IMA2018-054), the need to formalise a group for these minerals became clear. In the course of establishing the group, we re-examined the holotype kingsmountite specimen and found that the species corresponds to "aniyunwiyaite", which is herein discredited.

2. Background

Calcioferrite was the first of the minerals in this group to be described (Blum, 1858). Blum reported chemical analyses (wt%): Fe_2O_3 24.34, Al_2O_3 2.90, CaO 14.81, MgO 2.65, P_2O_5 34.01, H_2O 20.56, Σ99.27 and gave a measured density of 2.52 g cm^{-3}. On the basis of the Blum (1858) analyses, Palache *et al.* (1951) proposed the formula $Ca_3Fe_3(PO_4)_4(OH)_3{\cdot}8H_2O$ for calcioferrite. The second mineral to be described, montgomeryite, was assigned the ideal formula $Ca_4Al_5(PO_4)_6(OH)_5{\cdot}11H_2O$ by Larsen (1940). It was only when the crystal structure of

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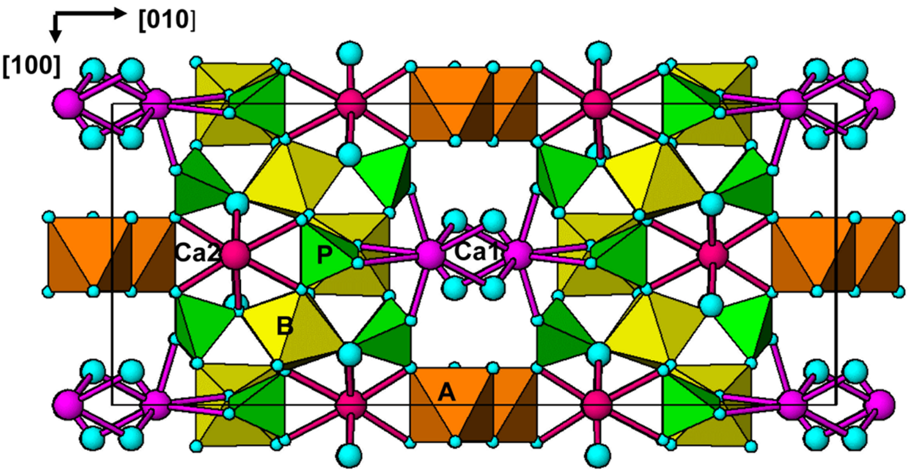

Fig. 1. [001] projection of monoclinic *C*2/*c* structure for $Ca_4AB_4(PO_4)_6(OH)_4{\cdot}12H_2O$ structures.

montgomeryite was determined by Moore & Araki (1974) that the correct formula $Ca_4MgAl_4(PO_4)_6(OH)_4{\cdot}12H_2O$ was proposed. Mead & Mrose (1968) had previously suggested that calcioferrite and montgomeryite are isostructural, but the correct ideal formula for calcioferrite, $Ca_4MgFe_4(PO_4)_6(OH)_4{\cdot}12H_2O$, was not presented until 1983 by Dunn *et al.* Kingsmountite, ideally $Ca_4FeAl_4(PO_4)_6(OH)_4{\cdot}12H_2O$, from the Foote mine, North Carolina, was identified and named by Dunn *et al.* (1979) as the Fe^{2+} analogue of montgomeryite. Those authors noted that individual crystals were extremely small and imperfect, and that a single-crystal study could not be undertaken. They noted, however, the close similarity of the PXRD pattern to that of montgomeryite and they refined *C*-centred monoclinic unit-cell parameters. In their 1983 paper, Dunn *et al.* reported that chemical analysis of a kingsmountite-like mineral from the Hagendorf pegmatite gave a formula corresponding ideally to $Ca_4MnFe_4(PO_4)_6(OH)_4{\cdot}12H_2O$. Dunn *et al.* (1988) subsequently described a mineral from Mangualde, Portugal, with composition similar to the Hagendorf mineral and named it zodacite. They confirmed the unit-cell symmetry and metrics using single-crystal methods and refined the cell parameters from the PXRD data.

Some doubt remains concerning the correct space group for these minerals. Moore & Araki (1974) refined the structure of montgomeryite from Fairfield, Utah, in space group *C*2/*c*. The structure is based on *zig-zag* 7 Å chains of corner-connected *B*-centred octahedra along [101] that are interconnected *via* PO_4 tetrahedra forming $[B_2(PO_4)_3(OH)_2]$ layers parallel to {010}, shown in projection in Fig. 1. Channels along [001] in the layers are occupied by Ca (site Ca2 in Fig. 1). The layers are connected *via* [001] edge-shared chains of $Ca1O_8$ polyhedra and AO_6 octahedra (A = Mg for montgomeryite). In the *C*2/*c* model, the *A* site is disordered with only 50% occupancy (Moore & Araki, 1974). Subsequently, Fanfani *et al.* (1976) reported that the diffraction patterns for montgomeryite from the same locality displayed weak additional reflections that violated the *c*-glide extinction condition. They refined the structure in *C*2. In the lower-symmetry space group, the *A* site splits into two independent sites and Fanfani *et al.* (1976) proposed that Mg was ordered in one of the two sites. It is possible, however, that the appearance of the very weak forbidden reflections was due to multiple diffraction, and any ordering is short-range. In their precession study of zodacite, Dunn *et al.* (1988) did not report any reflections violating the *c*-glide, and proposed that the space group is either *C*2/*c* or *Cc*. In a recent study on calcioferrite from the Moculta quarry, South Australia, Lafuente *et al.* (2014) obtained an excellent single-crystal refinement (R = 3.9%), with location of *H* atoms, based on the space group *C*2/*c*.

The two new minerals, fanfaniite (Grey *et al.*, 2018, 2019) and "aniyunwiyaite" (IMA2018-054) are both from the Foote lithium mine, North Carolina. Single-crystal refinements were conducted on both minerals. Fanfaniite refined satisfactorily in space group *C*2/*c*, but "aniyunwiyaite" has triclinic symmetry with a doubling of *a*. The superstructure along [100] was found to be due to ordering of octahedrally coordinated Mn^{2+} in one of the four independent eight-coordinated Ca sites in the triclinic structure.

3. New data on kingsmountite and "aniyunwiyaite" discredited

The "aniyunwiyaite" proposal was based on the characterization of specimens found in small dissolution cavities and along thin solution fractures in a partially altered spodumene-bearing pegmatite boulder on the eastern dump at the Foote mine, North Carolina (35°12′40″ N, 81° 21′20″ W). The mineral occurs as hemispherical radial aggregates, ~0.5–1 mm in diameter, consisting of transparent blades with widths 20–100 μm, lengths up to 500 μm and thickness generally < 5 μm (Fig. 2a). The blades are flattened on {010}, elongate on [001] and exhibit the forms {010}, {100} and {$20\bar{1}$}. They are flexible and elastic and have good cleavage on {010}. The measured indices of refraction, electron-microprobe analyses, density, unit-cell

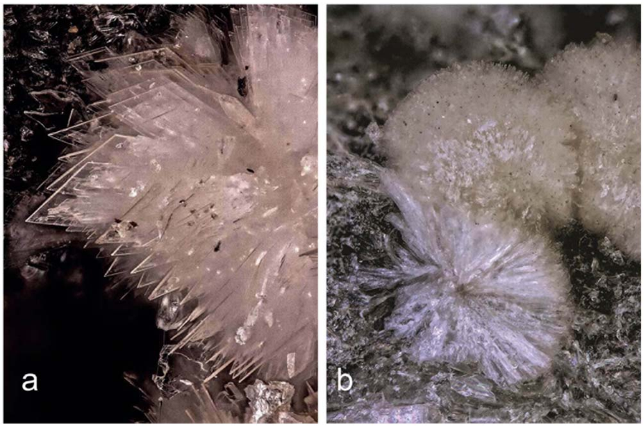

Fig. 2. Crystals of (a) "aniyunwiyaite" and (b) type kingsmountite.

parameters and PXRD lines for the mineral are compared with those for kingsmountite from the same locality (Dunn *et al.*, 1979) in Table 1.

The measured properties for the two minerals are almost identical. In addition to the *C*-centred monoclinic unit-cell parameters for kingsmountite in Table 1, we give the primitive cell parameters obtained by applying the transformation matrix (1 0 0, $\overline{0.5}$ 0.5 0, 0 0 1) for ease of comparison with the triclinic cell for "aniyunwiyaite". It is seen that there is a very close match of the two sets of cell parameters, and *a* for "aniyunwiyaite" is double that reported for kingsmountite (Dunn *et al.*, 1979), *i.e.* the "aniyunwiyaite" structure is a superstructure of the montgomeryite-type structure with a doubling of *a*. However, the monoclinic cell for kingsmountite was assumed and not verified by single-crystal studies (Dunn *et al.*, 1979). To check this we obtained the holotype specimen of kingsmountite.

In contrast to the well-developed crystals of "aniyunwiyaite", the type specimen of kingsmountite comprises hemispherules of poorly developed blades (Fig. 2b). Despite numerous attempts, we were not successful in locating crystals of type kingsmountite suitable for a single-crystal data collection. Dunn *et al.* (1979) had originally noted that even

Table 1. Comparison of kingsmountite and "aniyunwiyaite".

	Kingsmountite	"Aniyunwiyaite"
Chemical analyses		Average of 11 analyses SD in parentheses
CaO	14.9	14.6 (0.65)
MnO	8.1	6.56 (0.82)
MgO	0.2	0.45 (0.10)
ZnO	N.a.	0.29 (0.18)
FeO	4.1	3.33 (0.56)
Al_2O_3	16.7	15.8 (0.46)
P_2O_5	35.9	34.2 (0.95)
H_2O	20.6	21.3**
Empirical formula	$(Ca_{3.15}Mn_{0.85})(Fe^{2+}_{0.56}Mn_{0.50}Mg_{0.06})$ $(Al_{3.88}Fe_{0.12})(PO_4)_6(OH)_4\cdot 11.6H_2O$	$(Ca_{3.23}Mn_{0.77})(Fe^{2+}_{0.46}Mn_{0.38}Mg_{0.16})$ $(Al_{3.85}Fe_{0.12})(PO_4)_6(OH)_{3.83}\cdot 12.17H_2O$
Optics	Biaxial (–)	Biaxial (–)
α	1.575(3)	1.571(2)
β	1.581(3)	1.580(2)
γ	1.583(3)	1.581(2)
δ(meas)	2.51(3) g cm^{-3}	2.56(2) g cm^{-3}
Symmetry	Monoclinic, *C*2(?)	Triclinic, $P\bar{1}$
a, Å	10.029(6) (10.029)*	20.067(6)
b, Å	24.46(1) (13.218)	13.197(4)
c, Å	6.258(2) (6.258)	6.255(3)
α, °	90 (89.56)	89.35(2)
β, °	91.16(7) (91.16)	91.21(2)
γ, °	90 (112.29)	112.20(2)
PXRD		
d, I (hkl)	12.28, 50 (020)	12.28, 30 (010)
	6.33, 30 (130)	6.33, 14 (210, $\bar{2}20$)
	5.15, 100 (111)	5.15, 100 (201, $2\bar{1}1$)
	3.31, 30 (310, 170)	3.313, 13 ($\bar{6}20$, 230)
	2.95, 40 (311)	2.955, 39 ($\bar{6}11$)
	2.915, 30 (171)	2.913, 17 (231, $2\bar{4}1$)
	2.624, 60 (190)	2.630, 50 ($4\bar{1}2$, 430, $\bar{4}50$)
Reference	Dunn *et al.* (1979)	This study

**C*-centred monoclinic cell transformed to primitive cell using (1 0 0, $\overline{0.5}$ 0.5 0, 0 0 1).
**Calculated based on the structure containing 16 (OH + H_2O).

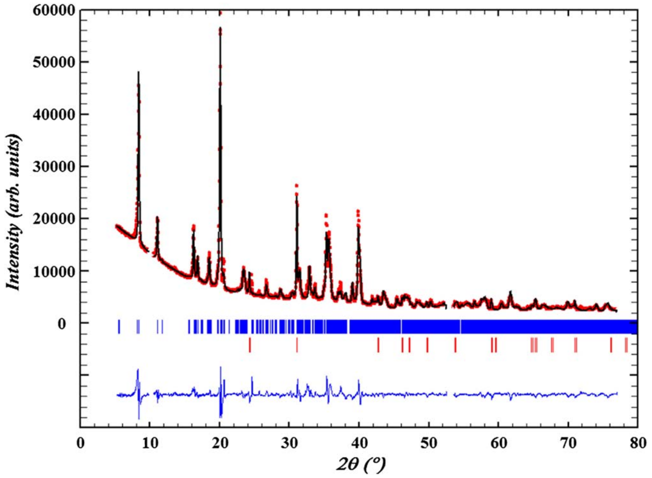

Fig. 3. Rietveld fit of type kingsmountite PXRD pattern using the triclinic "aniyunwiyaite" structure. Red tick marks are peak positions for quartz impurity.

the smallest elongate fibres that they could extract from the spherules gave uninterpretable single-crystal patterns. We then collected a PXRD pattern on ground spherules of type kingsmountite and conducted Rietveld refinements (Rodriguez-Carvajal, 1990) using atomic coordinates obtained from single-crystal refinements of both "aniyunwiyaite" (triclinic $P-1$) and fanfaniite, (monoclinic, $C2/c$). In both refinements, the coordinates were fixed at the single-crystal values and the same profile parameters were refined. The triclinic model gave a much better fit to the PXRD, with $R_{\mathrm{wp}} = 6.3\%$, $R_{\mathrm{Bragg}} = 8.9\%$, than the monoclinic model, with $R_{\mathrm{wp}} = 9.1\%$, $R_{\mathrm{Bragg}} = 15.2\%$. The powder pattern fitted by the triclinic model is shown in Fig. 3.

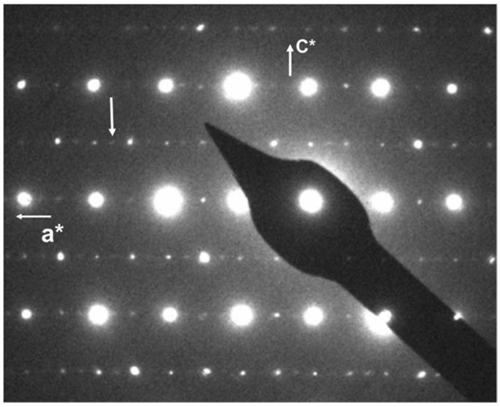

Fig. 4. Electron diffraction pattern for type kingsmountite. Arrow points to one of the superlattice reflections corresponding to $a = 20$ Å.

As a further check on the crystallography of type kingsmountite, we applied electron diffraction (ED). A ground spherule was sonicated and the crystals dispersed on a carbon grid for examination in a transmission electron microscope. Single blades were readily located, lying flat on the grid and giving ED patterns corresponding to a^*c^*. The ED patterns showed weak superlattice reflections corresponding to $a = 20$ Å, consistent with the cell of "aniyunwiyaite". An example ED pattern is shown in Fig. 4.

The results obtained for type kingsmountite are consistent with it having the crystal structure of "aniyunwiyaite". This information, coupled with the near-identical nature of the chemistry and optical properties leaves no doubt that "aniyunwiyaite" is kingsmountite and "aniyunwiyaite" is discredited. The discreditation of "aniyunwiyaite" and

Table 2. Crystal data and structure refinement for kingsmountite.

Formula (ideal)	$Ca_3Mn^{2+}Fe^{2+}Al_4(PO_4)_6(OH)_4{\cdot}12H_2O$
Formula weight	1192.8
Temperature	100 K
Wavelength	0.7107 Å
Space group	$P\bar{1}$
Unit-cell dimensions	$a = 20.067(6)$ Å, $\alpha = 89.35(2)°$ $b = 13.197(4)$ Å, $\beta = 91.21(2)°$ $c = 6.255(3)$ Å, $\gamma = 112.20(2)°$
Volume	1533.4(10) Å^3
Z	2
Absorption coefficient	1.90 mm^{-1}
Absorption correction	SADABS, $T_{\mathrm{min}}/T_{\mathrm{max}} = 0.51/0.75$
Crystal size	0.025 × 0.12 × 0.005 mm^3
θ range for data collection	1.1–32.2°
Index ranges	$-27 \leq h \leq 27$, $-17 \leq k \leq 17$, $-7 \leq l \leq 7$
Reflections collected	24,582
Independent reflections	5249 [$R_{\mathrm{int}} = 0.053$]
Reflections with $I_o > 3\sigma(I)$	4351
Refinement method	Full-matrix least-squares on F
Data resolution for refine	0.8 Å
Data/restraints/parameters	5249/0/522
Final R indices [$I > 3\sigma(I)$]	$R_{\mathrm{obs}} = 0.059$, $wR_{\mathrm{obs}} = 0.073$
R indices (all data)	$R_{\mathrm{obs}} = 0.069$, $wR_{\mathrm{obs}} = 0.075$
Largest diff. peak and hole	0.96 and -0.96 e·Å^{-3}

redefinition of kingsmountite have been approved by the IMA CNMNC (proposal 19-B). The crystallographic details in the following section, which were obtained for “aniyunwiyaite” are then those for kingsmountite.

4. Crystal structure of kingsmountite

The PXRD data for kingsmountite were obtained on a Rigaku R-Axis Rapid II curved–imaging-plate microdiffractometer utilising monochromatised Mo$K\alpha$ radiation. A Gandolfi-like motion on the φ and ω axes was used to randomize the sample. Observed d values and intensities were derived by profile fitting using JADE 2010 software (Materials Data Inc.). The unit-cell parameters refined from the powder data using JADE 2010 with whole-pattern fitting are a = 20.080(12), b = 13.188(12), c = 6.258(12) Å, α = 89.065(19), β = 91.285(13), γ = 112.20(2)° and V = 1534(3) Å^3. The indexed PXRD pattern is given in Table S1 of the Supplementary Material, linked to this article and freely available at https://pubs.geoscienceworld.org/eurjmin/.

A single-crystal data collection was made at the macromolecular beam line MX2 of the Australian Synchrotron. Data were collected using monochromatic radiation with a wavelength of 0.7107 Å. The crystal was maintained at 100 K in an open-flow nitrogen cryostream. Further data collection details are given in Table 2.

A structural model was obtained in space group $P\bar{1}$ using SHELXT (Sheldrick, 2015) and refined using JANA2006 (Petříček *et al.*, 2014). It was found to conform broadly to the monoclinic montgomeryite-type structure (Moore & Araki, 1974), but in the lower symmetry structure there are four crystallographically independent Ca sites, while there are only two independent Ca sites in the monoclinic structure. However, it was also noted that one of the four Ca sites is six- rather than eight-coordinated and has bond-distances consistent with occupancy by Mn^{2+} (Mn4 in Fig. 5). In addition, the half-occupied edge-sharing chains of interlayer octahedra in the monoclinic structure were found to be replaced by isolated octahedra with almost full occupancy (A in Fig. 5) in the triclinic crystal structure. Site-occupancy refinements, coupled with difference-Fourier maps, showed that the A site was only 85% occupied with 15% occupancy of an adjacent, edge-shared octahedron (A' in Table 3), and that the Mn4 site was 82% occupied with 18% occupation of an adjacent site displaced by 0.83 Å, which corresponds to a Ca site in montgomeryite. There was found to be the same (82/18%) partitioning of one of the H_2O molecules coordinated to Mn4 (Ow5/Ow5A in Table 3) to satisfy the coordination requirements of the adjacent Ca4. Minor (9%) partitioning of the Ca site Ca3 occurred into an adjacent site displaced by 0.86 Å. Mn was allocated to this site (Mn3 in Table 3). Although the electron microprobe (EMP) analyses showed a small (4%) deficiency in Al, site-occupancy refinements and bond valence sums (BVS, Gagné & Hawthorne, 2015) for the five independent Al sites gave no clear evidence for either vacancies or Fe^{3+} substitution for Al. The BVS for the A site indicated that this site was predominantly occupied by Fe^{2+}. Minor Mg from the EMP analysis and minor Mn were also included in the A site and the Fe occupancy was refined. The BVS for the minority A' site was consistent with it being occupied by Mn^{2+} (Table 3).

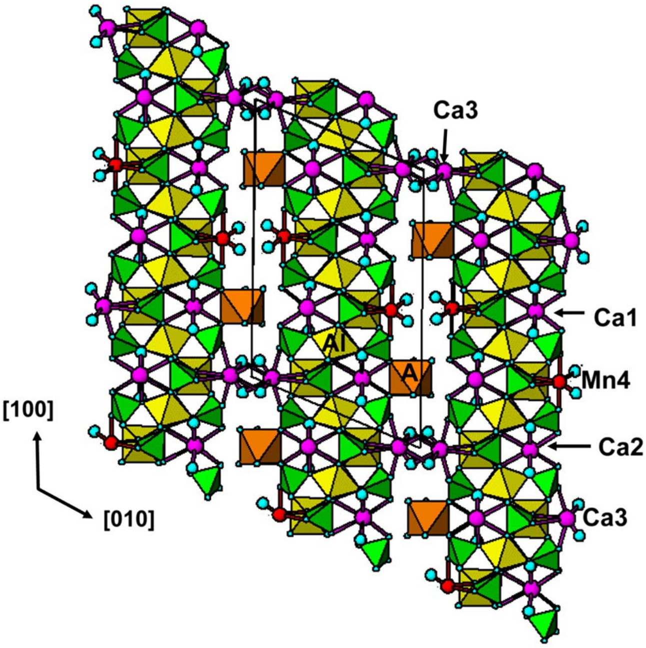

Fig. 5. [001] projection of triclinic kingsmountite structure.

Refinement with anisotropic displacement parameters for all atoms except the partially occupied sites A', Mn3, Ca4 and Ow5A converged at R_{obs} = 0.059 for 4351 reflections with $I > 3\sigma(I)$. Further details of the refinement are given in Table 2. The refined coordinates, equivalent isotropic displacement parameters and BVS values are reported in Table 3. Selected interatomic distances are reported in Table 4. The H atoms were not unambiguously located in difference-Fourier maps, but BVS values in Table 3 show clearly the presence of four hydroxyl ions, Oh1–Oh4, and 12 independent H_2O molecules, Ow1–Ow12. The Crystallography Information File (CIF), including reflection data, is available online as part of the Supplementary Material.

A [001] projection of the structure is shown in Fig. 5. As for montgomeryite, it is built from (010) heteropolyhedral slabs of corner-connected octahedra and tetrahedra, with composition $[Al_2(PO_4)_3(OH)_2]^{5-}$. Eight-coordinated Ca-centred polyhedra, $Ca1O_6(H_2O)_2$ and $Ca2O_6(H_2O)_2$, occupy cavities within the slabs, while eight-coordinated $Ca3O_4(H_2O)_4$, octahedrally coordinated $AO_2(H_2O)_4$ (A = dominant Fe^{2+}) and octahedrally coordinated $Mn4O_4(H_2O)_2$ occupy sites on the surface of the slabs. The $Ca3O_4(H_2O)_4$ polyhedra share edges *via* coordinated H_2O (Ow11 and Ow12) to form chains parallel to [001]. The A-centred octahedra are isolated, while the $Mn4O_4(H_2O)_2$ octahedra occur in pairs, as for Ca3, but are too far apart for edge-sharing as occurs for the Ca3-centred polyhedra.

Table 3. Refined coordinates, equivalent isotropic displacement parameters (Å^2), site occupation factors and bond valence sums for kingsmountite.

Atom	*sof*	*x*	*y*	*z*	U_{eq}	BVS
A	*	0.23916(5)	−0.05838(7)	0.75032(15)	0.0259(3)	2.00
A′	0.129(4)	0.2682(3)	−0.9413(4)	0.2477(10)	0.030(2)	2.05
Ca1	1	0.16332(5)	−0.34474(8)	0.74705(15)	0.0257(3)	2.11
Ca2	1	0.33189(5)	−0.67514(8)	0.24784(16)	0.0281(4)	2.00
Ca3	0.914(4)	0.02709(6)	−0.87735(11)	0.75023(17)	0.0254(5)	1.78
Mn3	0.086(4)	0.0420(4)	−0.8129(9)	0.7414(12)	0.019(3)	1.96
Ca4	0.177(5)	0.4679(3)	−0.1165(6)	0.2542(8)	0.0181(16)	2.27
Mn4	0.823(5)	0.44986(5)	−0.18082(10)	0.24110(16)	0.0320(5)	2.06
P1	1	0.09833(6)	−0.60209(9)	0.74460(19)	0.0236(4)	4.99
P2	1	0.18265(6)	−0.77381(9)	0.4484(2)	0.0250(4)	4.92
P3	1	−0.07306(6)	−0.76569(9)	0.0374(2)	0.0250(4)	4.98
P4	1	0.31135(6)	−0.24064(10)	0.5378(2)	0.0264(4)	4.99
P5	1	0.60528(6)	−0.58500(10)	0.7545(2)	0.0253(4)	4.96
P6	1	0.56311(6)	−0.23405(10)	0.9477(2)	0.0282(4)	4.99
Al1	1	0.08336(6)	−0.66000(10)	0.2440(2)	0.0206(5)	2.88
Al2	1	0.5	−0.5	0	0.0240(7)	3.09
Al3	1	0	−0.5	0	0.0224(7)	3.08
Al4	1	0.24674(6)	−0.50778(10)	0.49453(19)	0.0233(5)	3.06
Al5	1	0.40957(7)	−0.35298(11)	0.7445(2)	0.0225(5)	2.94
O1	1	0.06540(16)	−0.6752(3)	0.5524(5)	0.0276(11)	1.86
O2	1	0.09544(16)	−0.6760(2)	0.9381(5)	0.0273(12)	1.85
O3	1	0.17717(16)	−0.5251(3)	0.7042(5)	0.0280(12)	1.97
O4	1	0.05899(16)	−0.5243(3)	0.7898(5)	0.0269(12)	1.97
O5	1	0.14650(19)	−0.8327(3)	0.6515(6)	0.0348(13)	1.61
O6	1	0.22656(17)	−0.8311(3)	0.3400(6)	0.0292(12)	1.62
O7	1	0.23831(15)	−0.6578(3)	0.5076(5)	0.0261(11)	1.85
O8	1	0.12467(16)	−0.7665(3)	0.2892(5)	0.0279(12)	1.72
O9	1	−0.14465(17)	−0.8191(3)	0.1479(6)	0.0293(12)	1.90
O10	1	−0.06867(17)	−0.8221(3)	−0.1703(5)	0.0314(12)	1.62
O11	1	−0.01174(17)	−0.7647(3)	0.1931(5)	0.0292(12)	1.72
O12	1	−0.06791(15)	−0.6471(3)	−0.0075(5)	0.0252(11)	1.93
O13	1	0.26580(17)	−0.1844(3)	0.6348(6)	0.0318(12)	1.91
O14	1	0.34992(19)	−0.1830(3)	0.3363(6)	0.0402(14)	1.68
O15	1	0.25673(16)	−0.3571(3)	0.4808(5)	0.0276(12)	1.87
O16	1	0.36713(16)	−0.2485(3)	0.7046(5)	0.0290(12)	1.74
O17	1	0.68322(16)	−0.5078(3)	0.7150(5)	0.0270(11)	1.97
O18	1	0.56299(17)	−0.5117(3)	0.7946(6)	0.0310(12)	2.00
O19	1	0.57307(17)	−0.6620(3)	0.5637(5)	0.0288(12)	1.89
O20	1	0.60103(16)	−0.6616(3)	0.9466(5)	0.0278(12)	1.88
O21	1	0.63624(18)	−0.1729(3)	0.8503(6)	0.0358(13)	1.66
O22	1	0.5516(2)	−0.1773(3)	1.1464(6)	0.0451(16)	1.70
O23	1	0.50272(17)	−0.2450(3)	0.7803(5)	0.0293(12)	1.72
O24	1	0.56287(17)	−0.3481(3)	1.0111(5)	0.0293(12)	1.86
Oh1	1	0.04870(15)	−0.5447(2)	0.2186(5)	0.0222(11)	1.05
Oh2	1	0.44786(16)	−0.4633(3)	0.7795(5)	0.0239(11)	1.05
Oh3	1	0.17697(16)	−0.5480(3)	0.2742(5)	0.0275(12)	1.03
Oh4	1	0.31765(16)	−0.4677(3)	0.7122(5)	0.0269(11)	1.04
Ow1	1	0.2063(2)	0.0604(3)	0.9057(7)	0.0463(16)	0.29
Ow2	1	0.3030(2)	−1.0422(3)	0.0484(8)	0.0525(17)	0.29
Ow3	1	0.3317(2)	0.0641(3)	0.5987(7)	0.0493(16)	0.27
Ow4	1	0.18088(19)	−1.0411(3)	0.4540(7)	0.0420(15)	0.26
Ow5	0.81(2)	0.5118(4)	−0.0896(5)	0.4952(12)	0.055(3)	0.36
Ow5a	0.19(2)	0.5430(10)	−0.0513(16)	0.580(3)	0.016(6)	0.46
Ow6	1	0.4351(2)	−0.0811(4)	−0.0316(9)	0.074(2)	0.42
Ow7	1	0.08058(17)	−0.3478(3)	0.4741(5)	0.0302(12)	0.34
Ow8	1	0.24392(17)	−0.3480(3)	1.0223(6)	0.0354(14)	0.34
Ow9	1	0.25235(18)	−0.6659(3)	−0.0319(6)	0.0405(15)	0.32
Ow10	1	0.41618(19)	−0.6605(3)	0.5293(6)	0.0365(14)	0.32
Ow11	1	−0.04042(17)	−0.9434(3)	0.4174(6)	0.0332(13)	0.38
Ow12	1	0.06999(18)	−0.9514(3)	1.0746(6)	0.0351(13)	0.37

**A* site occupation = 0.568(4) Fe + 0.14 Mg + 0.14 Mn; *A*′ = 0.129(4) Mn.

Table 4. Polyhedral bond lengths for kingsmountite [Å].

A–O9	2.080(4)	*A*′–O6	2.026(6)
A–O13	2.071(3)	*A*′–O21	2.041(7)
A–Ow1	2.163(4)	*A*′–Ow1	2.456(7)
A–Ow2	2.206(5)	*A*′–Ow2	2.143(7)
A–Ow3	2.175(5)	*A*′–Ow3	2.503(7)
A–Ow4	2.226(4)	*A*′–Ow4	2.188(7)
Av.	2.153	Av.	2.226
Ca1–O3	2.517(4)	Ca2–O6	2.403(4)
Ca1–O4	2.516(4)	Ca2–O7	2.585(3)
Ca1–O9	2.429(4)	Ca2–O17	2.558(4)
Ca1–O12	2.510(3)	Ca2–O18	2.585(4)
Ca1–O13	2.437(4)	Ca2–O21	2.413(4)
Ca1–O15	2.585(3)	Ca2–O24	2.612(4)
Ca1–Ow7	2.346(4)	Ca2–Ow9	2.377(4)
Ca1–Ow8	2.348(4)	Ca2–Ow10	2.373(4)
Av.	2.461	Av.	2.488
Ca3–O1	2.766(4)	Mn4–O14	2.094(4)
Ca3–O2	2.751(4)	Mn4–O19	2.291(4)
Ca3–O5	2.336(4)	Mn4–O20	2.268(4)
Ca3–O10	2.362(3)	Mn4–O22	2.122(4)
Ca3–Ow11	2.441(4)	Mn4–Ow5	2.086(8)
Ca3–Ow11	2.704(4)	Mn4–Ow6	2.225(6)
Ca3–Ow12	2.516(4)	Av.	2.181
Ca3–Ow12	2.610(4)		
Av.	2.561	Al2–O18 ×2	1.869(3)
		Al2–O24 ×2	1.925(4)
Al1–O1	1.964(4)	Al2–Oh2 ×2	1.881(3)
Al1–O2	1.958(4)	Av.	1.892
Al1–O8	1.898(3)		
Al1–O11	1.909(4)	Al3–O4 ×2	1.896(3)
Al1–Oh1	1.901(3)	Al3–O12 ×2	1.904(3)
Al1–Oh3	1.909(4)	Al3–Oh1 ×2	1.880(3)
Av.	1.923	Av.	1.893
Al4–O3	1.884(4)	Al5–O16	1.886(3)
Al4–O7	1.923(4)	Al5–O19	1.960(4)
Al4–O15	1.923(4)	Al5–O20	1.968(4)
Al4–O17	1.895(3)	Al5–O23	1.885(4)
Al4–Oh3	1.875(4)	Al5–Oh2	1.895(3)
Al4–Oh4	1.877(4)	Al5–Oh4	1.901(4)
Av.	1.896	Av.	1.916
P1–O1	1.525(4)	P2–O5	1.528(4)
P1–O2	1.534(4)	P2–O6	1.533(3)
P1–O3	1.548(4)	P2–O7	1.560(4)
P1–O4	1.544(3)	P2–O8	1.545(3)
Av.	1.538	Av.	1.541
P3–O9	1.518(4)	P4–O13	1.517(3)
P3–O10	1.525(4)	P4–O14	1.530(4)
P3–O11	1.549(3)	P4–O15	1.553(4)
P3–O12	1.552(4)	P4–O16	1.545(3)
Av.	1.536	Av.	1.536
P5–O17	1.534(3)	P6–O21	1.519(4)
P5–O18	1.534(3)	P6–O22	1.524(4)
P5–O19	1.541(4)	P6–O23	1.550(3)
P5–O20	1.544(4)	P6–O24	1.550(4)
Av.	1.538	Av.	1.536

Kingsmountite is closely related, both compositionally and structurally, to the minerals calcioferrite, montgomeryite, zodacite and fanfaniite, which have the general formula $Ca_4AB_4(PO_4)_6(OH)_4 \cdot 12H_2O$ and *C*-centred monoclinic unit cells. If the unit cell for the *C*-centred monoclinic minerals is reduced to a primitive cell, the cell parameters are a ~ 10.0, b ~ 13.1, c ~ 6.2 Å, α ~ 89.5, β ~ 91.5, γ ~ 112.5°. A comparison with the cell parameters for triclinic kingsmountite shows that the latter has a doubled a cell parameter relative to the montgomeryite-type cell, with the other parameters almost the same for both minerals.

The triclinic kingsmountite superstructure of the monoclinic $Ca_4AB_4(PO_4)_6(OH)_4 \cdot 12H_2O$ structures results both from ordering of Mn in one of the Ca sites, and from ordering of the *A* cations. As shown in Fig. 5, along the lengths of the heteropolyhedral slabs, isolated *A*-centred octahedra alternate in position from one side of the slabs to the other, whereas in the *C*2/*c* structure (Fig. 1), edge-shared chains of half-occupied *A*-centred octahedra span the interlayer region between the slabs. The partially occupied sites *A*′, Mn3 and Ca4 in kingsmountite represent local disordered regions of the *C*2/*c*-type structure.

5. The calcioferrite group (Table 5)

The minerals calcioferrite, montgomeryite, kingsmountite, zodacite and fanfaniite meet the requirements for formation of a mineral group according to the definition given by Mills *et al.* (2009) that: *A mineral group consists of two or more minerals with the same or essentially the same structure, and composed of chemically similar elements*. Based on the recommendation by Mills *et al.* (2009) that the group name be that of the first mineral to be adequately characterized, the group name is calcioferrite (Blum, 1858). The general formula for the group members except for kingsmountite is $Ca_4AB_4(PO_4)_6(OH)_4 \cdot 12H_2O$. In kingsmountite, Ca_4 is replaced by Ca_3Mn. The group is subdivided into two subgroups based on the dominant trivalent B cation. The calcioferrite subgroup has $B = Fe^{3+}$ and the montgomeryite subgroup has $B = Al^{3+}$. Within each subgroup the different root-name minerals are distinguished by the dominant divalent A cation.

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Table 5. Minerals of the calcioferrite group.

General formula: $Ca_4AB_4(PO_4)_6(OH)_4 \cdot 12H_2O$				
	A^{2+}, B^{3+}	SG	Unit-cell parameters	Ref.
Calcioferrite Subgroup				
Calcioferrite	Mg, Fe^{3+}	*C*2/*c*	*a* = 10.1936(8), *b* = 24.196(2), *c* = 6.3218(4) Å, β = 91.161(4)°	1
Zodacite	Mn^{2+}, Fe^{3+}	*C*2/*c*	*a* = 10.152(8), *b* = 24.14(3), *c* = 6.308(6) Å, β = 91.14(7)°	2
Montgomeryite Subgroup				
Montgomeryite	Mg, Al	*C*2	*a* = 10.023(1), *b* = 24.121(3), *c* = 6.243(1) Å, β = 91.55(1)°	3, 4
Fanfaniite	Mn^{2+}, Al	*C*2/*c*	*a* = 10.032(5), *b* = 24.162(9), *c* = 6.241(2) Å, β = 91.47(2)°	5
Kingsmountite*	Fe^{2+}, Al	$P\bar{1}$**	*a* = 20.067(6), *b* = 13.197(4), *c* = 6.255(3) Å α = 89.35(2), β = 91.21(2), γ = 112.20(2)°	This study

*Kingsmountite has the general formula $Ca_3MnAB_4(PO_4)_6(OH)_4 \cdot 12H_2O$.

**The triclinic cell can be transformed to a pseudomonoclinic calcioferrite-type cell by the cell transformation $(0.5\ 0\ 0;\ \bar{0}.5\ \bar{2}\ 0;\ 0\ 0\ 1)$ giving *a* = 10.034, *b* = 24.44, *c* = 6.26 Å, α = 90.20, β = 91.21°, γ = 90.14°.

References: (1) Blum, 1858; (2) Dunn *et al.*, 1988; (3) Moore & Araki, 1974; (4) Fanfani *et al.*, 1976; (5) Grey *et al.*, 2018, 2019.

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References

Blum, J.R. (1858): Calcioferrit, eine neue Mineral-Spexies. *Neues Jahrb. Miner. Geog. Geol. Petrefaktenkunde*, 287–293.

Dunn, P.J., Peacor, D.A., White, J.S., Ramik, R.A. (1979): Kingsmountite, a new mineral isostructural with montgomeryite. *Can. Mineral.*, **17**, 579–582.

Dunn, P.J., Roberts, W.L., Campbell, T.J., Leavens, P.B. (1983): Red montgomeryite and associated minerals from the Tip Top Pegmatite with notes on kingsmountite and calcioferrite. *Miner. Rec.*, **14**, 195–197.

Dunn, P.J., Grice, J.D., Metropolis, W.C. (1988): Zodacite, the Mn analogue of montgomeryite, from Mangualde, Portugal. *Am. Mineral.* **73**, 1179–1181.

Fanfani, L., Nunzi, A., Zanazzi, P.F., Zanzari, A.R. (1976): Additional data on the crystal structure of montgomeryite. *Am. Mineral.*, **61**, 12–14.

Gagné, O.C. & Hawthorne, F.C. (2015): Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallogr. B*, **71**, 562–578.

Grey, I.E., Kampf, A.R., Smith, J.B., MacRae, C.M. (2018): Fanfaniite, IMA2018-053. CNMNC Newsletter No. 45, October 2018, page 1039. *Eur. J. Mineral.*, **30**, 1037–1043.

Grey, I.E., Kampf, A.R., Smith, J.B., MacRae, C.M., Keck, E. (2019): Fanfaniite, $Ca_4Mn^{2+}Al_4(PO_4)_6(OH,F)_4 \cdot 12H_2O$, a new mineral with a montgomeryite-type structure. *Eur. J. Mineral.*, **31**, 647–652. DOI: 10.1127/ejm/2019/0031-2857.

Lafuente, B., Downs, R.T., Yang, H., Jenkins, R.A. (2014): Calcioferrite with composition $(Ca_{3.94}Sr_{0.06})Mg_{1.01}(Fe_{2.93}Al_{1.07})(PO_4)_6(OH)_4 \cdot 12H_2O$. *Acta Crystallogr.*, **E70**, 116–117.

Larsen, E.S. (1940): Overite and montgomeryite: two new minerals from Fairfield, Utah. *Am. Mineral.*, **25**, 315–326.

Mead, C.W. & Mrose, M.E. (1968): Solving problems in phosphate mineralogy with the electron probe. *U.S. Geol. Surv. Prof. Paper*, **600-D**, D204–D206.

Mills, S.J., Hatert, F.H., Nickel, E.H., Ferraris, G. (2009): The standardisation of mineral group hierarchies: application to recent nomenclature proposals. *Eur. J. Mineral.*, **21**, 1073–1080.

Moore, P.B. & Araki, T. (1974): Montgomeryite, $Ca_4Mg(H_2O)_{12}[Al_4(OH)_4(PO_4)_6]$: its crystal structure and relation to vauxite, $Fe_2^{2+}(H_2O)_4[Al_4(OH)_4(H_2O)_4(PO_4)_4] \cdot 4H_2O$. *Am. Mineral.*, **59**, 843–950.

Palache, C., Berman, H., Frondel, C. (1951): The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana, Yale University 1837–1892, Volume II, 7th edition. John Wiley and Sons Inc, New York, 976–977pp.

Petříček, V., Dušek, M., Palatinus, L. (2014): Crystallographic computing system JANA2006: general features. *Z. Krisallogr.*, **229**, 345–352.

Rodriguez-Carvajal, J. (1990): FULLPROF: a program for rietveld refinement and pattern matching analysis. Satellite meeting on powder diffraction of the XV Congress of the IUCr, Toulouse, France, 1990.

Sheldrick, G.M. (2015): Crystal structure refinement with *SHELXL*. *Acta Crystallogr. C*, **71**, 3–8.

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