



Article

Manganoarrojadite-(KNa), $\text{KNa}_5\text{MnFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$, a new arrojadite-group mineral from the Palermo No. 1 mine, New Hampshire, USA

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Abstract

A new arrojadite-group mineral manganoarrojadite-(KNa), ideally $\text{KNa}_5\text{MnFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$, was found in a phosphate-bearing granite pegmatite at the Palermo No. 1 mine, New Hampshire, USA. It forms anhedral grains up to 1×1.5 cm in size combined in aggregates with vivianite, goyazite, quartz and calcite. The mineral is olive green with a pale green streak and vitreous to greasy lustre. The cleavage is good in one direction. The Mohs hardness is $4\frac{1}{2}$. D_{calc} is 3.53 g/cm^3 . Manganoarrojadite-(KNa) is optically biaxial (-), $\alpha = 1.658(2)$, $\beta = 1.666(2)$, $\gamma = 1.670(2)$, $2V_{\text{meas.}} = 67(1)^\circ$ and $2V_{\text{calc.}} = 70^\circ$ (589 nm). The infrared spectrum is reported. The composition (wt.%) is Na_2O 6.97, K_2O 1.78, CaO 0.31, MgO 2.17, MnO 12.30, FeO 31.17, Al_2O_3 2.43, P_2O_5 40.48, F 0.30, H_2O 1.32, $\text{O} = \text{F}_2$ -0.13, total 99.10. The empirical formula calculated on the basis of 12 P and $(\text{O} + \text{OH} + \text{F}) = 50$ apfu is $\text{Na}_{4.73}\text{K}_{0.80}\text{Ca}_{0.12}\text{Mg}_{1.13}\text{Mn}_{3.65}^{2+}\text{Fe}_{9.13}^{2+}\text{Al}_{1.00}\text{P}_{12.00}\text{O}_{46.59}\text{OH}_{3.08}\text{F}_{0.33}$. The ideal structural formula is ${}^{\text{A1}}\text{K}^{\text{A2}}\text{Na}^{\text{B1}}\text{Na}^{\text{B2}}\text{Na}^{\text{Na1,2}}\text{Na}_2^{\text{Na3}}\square^{\text{C}}\text{Mn}^{\text{M}}\text{Fe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})^{\text{W}}(\text{OH})_2$. The mineral is monoclinic, Cc , $a = 16.5345(3)$, $b = 10.0406(2)$, $c = 24.6261(5)$ Å, $\beta = 105.891(2)^\circ$, $V = 3932.09(14)$ Å³ and $Z = 4$. The strongest reflections of the powder X-ray diffraction pattern [d , Å(I)(hkl)] are: 5.902(24)(202), 5.025(24)(020), 3.208(47)(206, $\bar{1}32$), 3.048(100)($\bar{5}14$, $\bar{4}24$), 2.758(24)($\bar{6}02$) and 2.704(70)(226). The crystal structure, refined from single-crystal X-ray diffraction data ($R_1 = 0.025$), is of the arrojadite structure type. Manganoarrojadite-(KNa) is the first arrojadite-group mineral with Mn dominant on the site usually occupied by Ca and without Ca as the dominant cation at any cation site.

Keywords: manganoarrojadite-(KNa), new mineral, arrojadite group, crystal structure, pegmatite, Palermo No. 1 mine, USA

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Introduction

Arrojadite-group minerals are complex primary pegmatite phosphates with the general structural formula $\text{A}_2\text{B}_2\text{CNa}_{2+x}\text{M}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH}_{1-x})\text{W}_2$ (after Cámara *et al.*, 2006; with the Ca site labelled as C). Eleven members of the group are currently known on the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) list (Pasero, 2020). Following the IMA-accepted nomenclature (Chopin *et al.*, 2006), they are named according to the combination of the predominant cations at the M sites [rootname; Fe^{2+} – arrojadite, Mn^{2+} – dickinsonite (Chopin *et al.*, 2006) and Mg – carmoite (Cámara *et al.*, 2019)] and the dominant cation of the dominant valence state at the A1 and B1 sites [two suffix-modifiers, e.g. arrojadite-(KNa)]. A third suffix is added in case the sum of non-(P,Al) cations exceeds 20.5 atoms per formula unit (apfu) [which implies that the Na3 site is more than half occupied, e.g. dickinsonite-(KMnNa)] and prefixes may be added to the rootname in the case of dominance

of F over OH at the W site or of Fe^{3+} over Al at the Al site [e.g. fluorarrojadite-(BaFe)]. The nomenclature also proposed handling potential monovalent substitutions at the C site in the same way as for the Al site, i.e. by using an appropriate prefix like bario- or strontio-.

Manganoarrojadite-(KNa), ideally $\text{KNa}_5\text{MnFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$, is a new member of the arrojadite group described in this paper. It was found while examining a specimen labelled 'dickinsonite-(KMnNa)' in the collection of the Canadian Museum of Nature, Ottawa, Canada (CMNMC 47194). Manganoarrojadite-(KNa) was named in accordance with the IMA nomenclature of the arrojadite group (Chopin *et al.*, 2006) as a mineral with Fe^{2+} as the dominant cation at the M sites [rootname arrojadite], K at the A1 site, Na at the B1 site site [two suffix-modifiers (KNa)] and Mn^{2+} at the C site [prefix mangano-]. Both the new mineral and the name have been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification, proposal IMA2020-003 (Lykova *et al.*, 2020). The specimen CMNMC 47194 became the holotype of manganoarrojadite-(KNa).

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Occurrence and general appearance

Manganoarrojadite-(KNa) occurs at the Palermo No. 1 mine, Grafton Co., New Hampshire, USA. The mine exploited a large

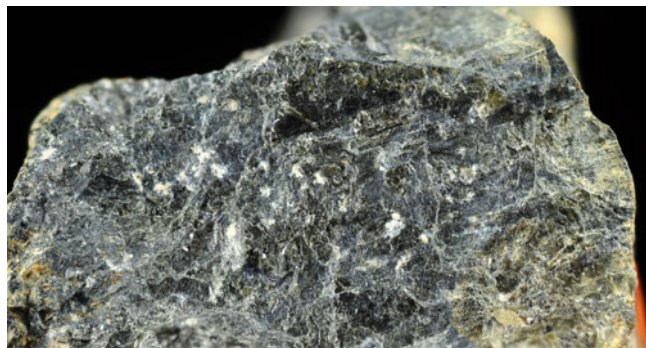


Fig. 1. Olive-green manganoarroyadite-(KNa) partially replaced by vivianite, which causes the bluish-grey shade. White grains are goyazite. Field of view = 2.2 cm. Specimen CMNMC 47194. Photo: John Montgomery.

phosphate-bearing granite pegmatite and is famous worldwide as a source of numerous rare primary and secondary phosphates (Segeler *et al.*, 1981; Whitmore and Lawrence, 2004). The new mineral forms anhedral slightly elongated grains up to 1 cm × 1.5 cm in size (Fig. 1) combined in aggregates. Manganoarroyadite-(KNa) was partially replaced along intergrain fractures by vivianite $\text{Fe}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Fig. 2) during late stages of the pegmatite formation. The other associated minerals are goyazite $\text{SrAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6$, quartz and calcite.

Physical and optical properties

In separate grains manganoarroyadite-(KNa) is olive green with a pale green streak and vitreous to greasy lustre. In aggregates it is grey-green and bluish-grey due to the vivianite inclusions (Fig. 1). The cleavage is good in one direction [probably {001}]. The Mohs hardness is 4½. The fracture is uneven, stepped. The mineral is non-fluorescent under ultraviolet light. The density calculated using the empirical formula and unit-cell volume refined from the single-crystal X-ray diffraction (XRD) data is 3.53 g/cm³.

Manganoarroyadite-(KNa) is optically biaxial (-), $\alpha = 1.658(2)$, $\beta = 1.666(2)$, $\gamma = 1.670(2)$, $2V_{\text{meas.}} = 67(1)^\circ$ (from a spindle-stage extinction curve) and $2V_{\text{calc.}} = 70^\circ$ (589 nm). Pleochroism is very weak and the absorption scheme is as follows: $X \approx Y$ very pale green < Z pale green.

Experimental methods

Chemical data for manganoarroyadite-(KNa) were obtained using a JEOL 8230 SuperProbe electron microscope equipped with five wavelength dispersive spectrometers (University of Ottawa – Canadian Museum of Nature MicroAnalysis Laboratory, Canada) with an acceleration voltage of 20 kV, a beam current of 10 nA and a beam diameter of 20 µm. The following reference materials were used: albite (Na), sanidine (K and Al), fluorapatite (Ca, P and F), diopside (Mg), tephroite (Mn) and hematite (Fe). The intensity data were corrected for Time Dependent Intensity (TDI) loss (or gain) using a self-calibrated correction for $\text{K}\alpha$, $\text{Na}\alpha$, $\text{Fe}\alpha$, $\text{F}\alpha$ and $\text{P}\alpha$.

The Fourier-transform infrared (FTIR) spectrum of manganoarroyadite-(KNa) was obtained at the Canadian Conservation Institute, Canada using a Bruker Hyperion 2000 microscope interfaced to a Tensor 27 spectrometer with a wide-band mercury cadmium telluride (MCT) detector. A small fragment of manganoarroyadite-(KNa) was mounted on a low-pressure

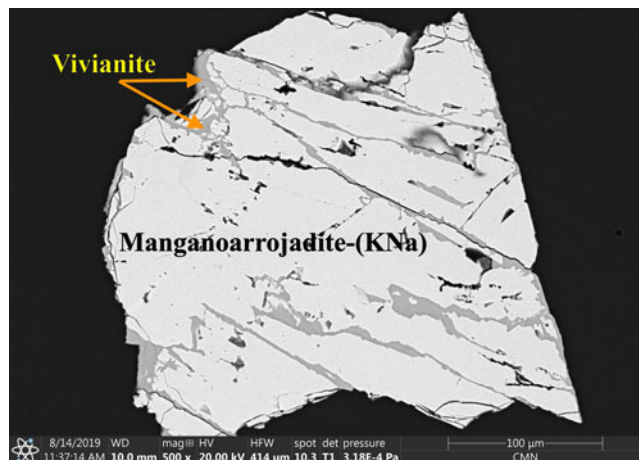


Fig. 2. Manganoarroyadite-(KNa) partially replaced by vivianite. Polished section. Back-scattered electron image.

Table 1. Compositional results (in wt.%, average of 11 analyses) for manganoarroyadite-(KNa).

Constituent	Mean	Range	S.D.
Na ₂ O	6.97	6.65–7.41	0.21
K ₂ O	1.78	1.65–1.94	0.09
CaO	0.31	0.10–0.72	0.17
MgO	2.17	1.95–2.54	0.20
MnO	12.30	11.39–13.30	0.59
FeO	31.17	29.64–32.50	0.79
Al ₂ O ₃	2.43	2.15–2.79	0.18
P ₂ O ₅	40.48	39.53–41.42	0.66
F	0.30	0.12–0.62	0.16
H ₂ O*	1.32		
-O = F ₂	-0.13		
Total	99.10		

*calculated from stoichiometry; S.D. – standard deviation.

diamond anvil microsample cell and analysed in transmission mode. The spectrum was collected between 400–4000 cm⁻¹ with the co-addition of 150 scans at a 4 cm⁻¹ resolution.

Powder XRD data were collected at the Canadian Museum of Nature, Canada using a Bruker D8 Discover microdiffractometer equipped with a DECTRIS EIGER2 R 500K detector and IµS microfocus X-ray source ($\lambda\text{CuK}\alpha = 1.54184 \text{ \AA}$). The instrument was calibrated using a statistical calibration method (Rowe, 2009). A powder ball 200 µm in diameter, mounted on a fibre pin mount, was analysed with continuous Phi rotation and 10° rocking motion along the Psi axis of the Centric Eulerian Cradle stage.

Single-crystal X-ray studies were carried out at room temperature on a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix 6000HE detector ($\lambda\text{MoK}\alpha = 0.71073 \text{ \AA}$) operating at 50 kV and 1 mA, housed at the Natural History Museum, University of Oslo, Norway. The data were processed, including face indexed absorption correction, using Rigaku's *CrysAlis Pro* software.

Results

Chemical data

Chemical data for manganoarroyadite-(KNa) are given in Table 1. The data based on 11 analyses of four crystal fragments from

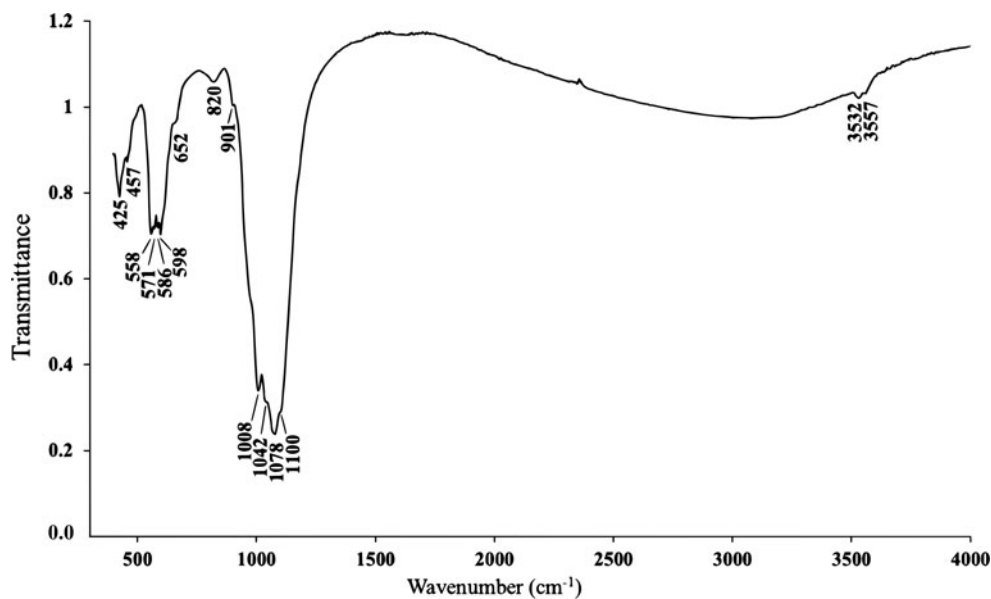


Fig. 3. Infrared spectrum of manganorrodite-(KNa).

Table 2. Powder X-ray diffraction (d in Å) data for manganorrodite-(KNa).

$l_{\text{obs.}}$	$d_{\text{obs.}}$	$l_{\text{calc.}}^1$	$d_{\text{calc.}}^2$	hkl	$l_{\text{obs.}}$	$d_{\text{obs.}}$	$l_{\text{calc.}}^1$	$d_{\text{calc.}}^2$	hkl
6	11.87	8	11.87	002	20	2.545	20	2.545	424
6	8.50	7	8.50	110	16	2.513	19	2.513	040
6	7.95	5	7.97	200	4	2.470	3	2.469	$\bar{2}$.0.10
17	7.66	17	7.67	$\bar{2}$ 02	13	2.429	14	2.429	$\bar{4}$ 28
6	7.45	4	7.45	$\bar{1}$ 12	13	2.418	13	2.418	622
15	6.47	15	6.48	112	8	2.392	7	2.392	$\bar{6}$ 24
12	5.932	9	5.935	004	4	2.344	2	2.344	625
24	5.902	23	5.903	202	3	2.317	2	2.314	044
14	5.546	18	5.549	204	7	2.309	5	2.309	530
4	5.248	2	5.243	$\bar{1}$ 14	5	2.272	2	2.271	318
24	5.025	27	5.027	020	5	2.264	5	2.262	535
4	4.784	3	4.784	$\bar{3}$ 12	6	2.222	4	2.221	045
4	4.693	3	4.675	310	10	2.206	8	2.206	$\bar{7}$ 16
8	4.629	8	4.629	022	5	2.147	3	2.147	0.2.10
13	4.559	10	4.561	114	5	2.123	2	2.122	046
6	4.135	5	4.135	$\bar{4}$ 02	7	2.117	3, 2, 2	2.120, 2.116, 2.116	2.0.10, 408, $\bar{5}$ 37
5	3.981	2	3.983	400	3	2.103	3	2.102	444
6	3.471	3	3.472	$\bar{7}$ 16	5	1.9917	4	1.9912	800
5	3.450	3	3.452	025	7	1.9785	4	1.9785	$\bar{1}$ 52
21	3.401	20	3.401	116	9	1.9515	7, 6	1.9538, 1.9503	2.2.10, 428
13	3.308	11	3.310	314	4	1.9453	3	1.9453	248
5	3.281	5	3.279	130	11	1.9165	2, 8, 2, 3	1.9179, 1.9162, 1.9135, 1.9135	048, $\bar{8}$ 08, 444, 338
5	3.237	4	3.237	224	5	1.8832	3, 3	1.8859, 1.8826	352, 730
47	3.208	33, 17	3.208, 3.208	206, $\bar{1}$32	3	1.8630	3	1.8628	$\bar{4}$ 48
8	3.138	5	3.137	17	5	1.8578	3, 2	1.8577, 1.8537	642, $\bar{3}$.3.11
7	3.118	2, 4	3.118, 3.116	$\bar{5}$ 11, 132	4	1.7903	3, 2, 3	1.7969, 1.7905	732, $\bar{8}$ 28, $\bar{8}$.0.10
100	3.048	8, 100	3.048, 3.048	514, 424	13	1.7616	10, 7	1.7615, 1.7605	2.4.10, 2.0.14
5	2.938	2, 3	2.940, 2.933	$\bar{1}$ 18, $\bar{5}$ 15	11	1.7550	2, 11	1.7570, 1.7547	156, 642
5	2.871	4	2.870	422	5	1.7472	3, 3	1.7478, 1.7475	804, $\bar{3}$.3.12
20	2.853	21	2.853	$\bar{3}$ 32	2	1.7371	3	1.7360	$\bar{6}$.2.12
12	2.839	9, 9	2.841, 2.834	318, 330	3	1.7143	4	1.7140	4.4.10
13	2.804	11	2.804	134	3	1.7010	2	1.7004	550
18	2.790	18	2.790	516	6	1.6831	6	1.6827	158
20	2.775	19	2.775	$\bar{4}$ 08	5	1.6615	2, 5, 4	1.6636, 1.6616, 1.6591	$\bar{3}$ 58, $\bar{2}$.2.14, 062
24	2.758	22	2.758	602	10	1.6513	3, 3, 7	1.6531, 1.6529, 1.6509	556, 1.3.12, 824
10	2.717	3, 3	2.718, 2.716	$\bar{3}$ 34, 316	7	1.6043	7	1.6041	4.0.12
70	2.704	81	2.704	226	9	1.5678	6, 3	1.5677, 1.5672	6.0.10, $\bar{8}$.2.12
7	2.669	5	2.669	332	5	1.5616	4	1.5618	$\bar{1}$ 0.2.6
9	2.600	9	2.599	$\bar{1}$ 36	4	1.5355	4	1.5353	464
15	2.556	9, 6	2.556, 2.555	028, $\bar{6}$ 06	6	1.5281	3	1.5282	4.2.12

¹Calculated from the crystal structure determination, only reflections with intensities ≥ 1 are given.

²Calculated from PXRD Rietveld unit-cell refinement with $a = 16.5732(2)$, $b = 10.0535(1)$, $c = 24.7002(2)$ Å, $\beta = 106.0253(7)^\circ$ and $V = 3955.60(7)$ Å³.

The strongest lines are given in bold.

different parts of the specimen show that the mineral is homogeneous. One of the analysed fragments was later used for the crystal-structure study. The empirical formula calculated on the basis of 12 P and (O+OH+F) = 50 apfu is $\text{Na}_{4.73}\text{K}_{0.80}\text{Ca}_{0.12}\text{Mg}_{1.13}\text{Mn}_{3.65}\text{Fe}_{9.13}\text{Al}_{1.00}\text{P}_{12.00}\text{O}_{46.59}\text{OH}_{3.08}\text{F}_{0.33}$. The O/OH ratio was calculated by the charge balance. All Fe was assumed to be 2+.

The simplified formula is $\text{KNa}_5\text{Mn}^{2+}(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$. The end-member formula is $\text{KNa}_5\text{MnFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$, which requires K_2O 2.20, Na_2O 7.25, MnO 3.32, FeO 43.71, Al_2O_3 2.39, P_2O_5 39.86, H_2O 1.27, total 100 wt.%.

Manganoarrojadite-(KNa) does not react with a diluted aqueous HCl solution at room temperature.

Infrared spectroscopy

The infrared (IR) spectrum of manganoarrojadite-(KNa) (Fig. 3) shows IR bands of O–H stretching (in the range from 3530 to 3560 cm^{-1}) and P–O stretching (1000–1100 cm^{-1}) vibrations. The bands in the ranges 560–650 and 425–460 cm^{-1} correspond to M–O stretching vibrations where $M = \text{Fe}, \text{Mn}, \text{Mg}$ and Al . The weak band at 901 cm^{-1} can be explained by the presence of acid orthophosphate groups, confirming structural data that show protonation of O7 and, partially, of O30 and O31 (see below). The band assignment was made in accordance with Chukanov and Chervonnyi (2016).

Characteristic bands of H–O–H bending vibrations of H_2O molecules (in the range 1550–1750 cm^{-1}) and CO_3^{2-} anions (in the range 1350–1550 cm^{-1}) are absent in the IR spectrum of manganoarrojadite-(KNa). The presence of NH_4^+ groups, previously reported in arrojadite-(KNa) from Rapid Creek, Yukon, Canada (Della Ventura *et al.*, 2014), can also be excluded due to the absence of bands of H–O–H bending vibrations of NH_4^+ molecules in the range 1400–1440 cm^{-1} .

X-ray diffraction data and description of the crystal structure

The indexed powder XRD data are given in Table 2. Parameters of the monoclinic unit cell refined from the powder data are as follows: $a = 16.5732(2)$, $b = 10.0535(1)$, $c = 24.7002(2)$ Å, $\beta = 106.025(1)^\circ$ and $V = 3955.60(7)$ Å³.

The single-crystal XRD data were indexed in the Cc space group with the following unit-cell parameters: $a = 16.5345(3)$, $b = 10.0406(2)$, $c = 24.6261(5)$ Å, $\beta = 105.891(2)^\circ$ and $V = 3932.09(14)$ Å³. The structure was refined to $R_1 = 0.025$ on the basis of 8515 independent reflections with $I > 2\sigma(I)$ using the *SHELXL-2018/3* program package (Sheldrick, 2015). The atomic coordinates of arrojadite-(KNa) (Cámara *et al.*, 2006) were used as a starting model for the refinement. Crystal data, data collection and structure-refinement details are given in Table 3, atom coordinates, equivalent displacement parameters, site occupancy factors and bond valence sums (BVS) in Table 4 and selected interatomic distances in Table 5. The studied crystal of manganoarrojadite-(KNa) demonstrated twinning by merohedry Class I (Nespolo and Ferraris, 2000), with a twin domain ratio of 96:4. The crystallographic information file for manganoarrojadite-(KNa) has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below). It was also

Table 3. Crystal data, data collection information and structure refinement details for manganoarrojadite-(KNa).

Crystal data	
Ideal formula	$\text{KNa}_5\text{MnFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$
Crystal dimensions (mm)	0.019 × 0.040 × 0.058
Crystal system, space group	Monoclinic, Cc
a, b, c (Å)	16.5345(3), 10.0406(2), 24.6261(5)
β (°)	105.891(2)
V (Å ³)	3932.09(14)
Z	4
Calculated density (g cm^{-3})	3.53
μ (mm^{-1})	5.23
Data collection	
Crystal description	Pale green anhedral grain
Instrument	Rigaku XtaLAB Synergy-S
Radiation type, wavelength (Å)	$\text{MoK}\alpha$, 0.71073
Number of frames	1327
θ range (°)	2.40–33.39
Absorption correction	<i>CrysAlisPro</i> (Rigaku Oxford Diffraction, 2019)
$T_{\text{min}}, T_{\text{max}}$	0.816, 0.965
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21717, 8918, 8515
R_{int}	0.0178
Data completeness to $33.39^\circ\theta$ (%)	99.9
Indices range of h, k, l	$-23 \leq h \leq 25, -14 \leq k \leq 14, -20 \leq l \leq 35$
Refinement	
Refinement	Full-matrix least squares on F^2
Number of reflections, parameters, restraints	8918, 751, 2
R_1 [$I > 2\sigma$], R_1 (all)	0.025, 0.027
wR_2 [$I > 2\sigma$], wR_2 (all)	0.065, 0.066
GoF	1.029
No. of refined parameters	751
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ ($e^- \text{Å}^{-3}$)	1.88 / -0.88

deposited in the Inorganic Crystal Structure Database (ICSD; #CSD 2042959).

The crystal structure of manganoarrojadite-(KNa) is based on a framework of P-centred tetrahedra, five- and six coordinated M cations, and Al-centred octahedra linked together *via* common vertices (Fig. 4). There are 13 independent M sites in the structure. Fe, Mn and Mg atoms are distributed among these sites based on the microprobe data and refined site-scattering factors (e_{ref} , in electrons per site) taking into account BVS and interatomic distances (Tables 4, 5). For example, the sites Fe4 and Fe5 with the lowest e_{ref} values (20.8 and 20.6, respectively) are characterised by a significant admixture of Mg atoms (30% of the site occupancy), whereas the Fe10, Mn11 and Mn13 sites form the largest M -centred polyhedra with the average $\langle M\text{--O} \rangle$ distances of 2.220, 2.228 and 2.226 Å, respectively, and thus characterised by a significant presence of Mn atoms (40, 60 and 60% of the occupancy, respectively). According to arrojadite-group nomenclature (Chopin *et al.*, 2006), only the dominant cation among all the M sites taken as a bulk is considered when choosing the root name. Therefore, manganoarrojadite-(KNa) belongs to the Fe-dominant arrojadite series. One Al and 13 P sites are fully occupied.

There are five independent Na sites, four fully occupied and one partially occupied [Na5 with the occupancy of 75%], and one K site with an occupancy of 88%.

The Mn site [= the Ca site according to the nomenclature by Chopin *et al.* (2006)] is occupied by $0.88\text{Mn}^{2+} + 0.12\text{Ca}$ [$e_{\text{ref}} = 24.3$] with the average $\langle \text{Mn--O} \rangle$ distance of 2.286 Å. The bond-valence sum (BVS) at the Mn site is 1.74 valence units (vu, Table 4). The interatomic distances and the BVS unambiguously

Table 4. Coordinates and equivalent displacement parameters (U_{eq} , in Å²) of atoms, site occupancy factors (s.o.f.) and bond-valence sums for manganoarroyadite-(KNa).

Site	Site2 ¹	x/a	y/b	z/c	U_{eq}	s.o.f./site composition ²	BVS ³
K	A1	0.99862(13)	0.50858(13)	0.24413(10)	0.0352(5)	K _{0.874(6)}	0.95
Na1	A2	0.0040(2)	0.9977(2)	0.99843(13)	0.0228(4)	Na _{1.00}	1.14
Na2	B1	0.8736(3)	0.4867(2)	0.87784(12)	0.0443(9)	Na _{1.00}	1.11
Na3	B2	0.29495(15)	0.4459(2)	0.04226(10)	0.0277(5)	Na _{1.00}	0.87
Na4	Na1	0.12151(18)	0.5116(2)	0.12095(10)	0.0221(5)	Na _{1.00}	1.23
Na5	Na2	0.02189(19)	0.8183(3)	0.77109(12)	0.0258(9)	Na _{0.752(9)}	0.59
Mn	C	0.23041(5)	0.78586(6)	0.97856(3)	0.01277(12)	[24.3] Mn _{0.88} Ca _{0.12}	1.74
Fe1	M1	0.22726(4)	0.11699(6)	0.97591(3)	0.01155(11)	[25.2] Fe _{0.70} Mn _{0.30}	1.96
Fe2	M2a	0.28938(5)	0.51216(7)	0.22829(3)	0.01184(14)	[23.6] Fe _{0.55} Mn _{0.30} Mg _{0.15}	1.82
Fe3	M2b	0.71499(5)	0.49329(7)	0.76594(3)	0.01128(13)	[25.0] Fe _{0.70} Mn _{0.30}	1.94
Fe4	M3a	0.11254(5)	0.10474(8)	0.13706(4)	0.01063(15)	[20.8] Fe _{0.70} Mg _{0.30}	2.15
Fe5	M3b	0.89613(6)	0.98862(8)	0.85777(4)	0.01060(15)	[20.6] Fe _{0.70} Mg _{0.30}	2.07
Fe6	M4a	0.02154(4)	0.75148(7)	0.90041(3)	0.00914(13)	[24.2] Fe _{0.90} Mg _{0.10}	2.07
Fe7	M4b	0.97754(4)	0.24724(7)	0.09333(3)	0.00769(13)	[23.7] Fe _{0.85} Mg _{0.15}	2.06
Fe8	M5a	0.96960(4)	0.74714(6)	0.09624(3)	0.00800(12)	Fe _{1.00}	1.99
Fe9	M5b	0.03563(4)	0.26024(7)	0.89825(3)	0.00847(12)	Fe _{1.00}	1.99
Fe10	M6a	0.20642(4)	0.30592(7)	0.84961(3)	0.01099(13)	[24.8] Fe _{0.60} Mn _{0.40}	1.79
Mn11	M6b	0.29818(5)	0.19937(8)	0.14574(3)	0.01431(15)	[24.9] Mn _{0.60} Fe _{0.40}	1.85
Fe12	M7a	0.28452(4)	0.78871(7)	0.15165(3)	0.00970(13)	[24.1] Fe _{0.60} Mn _{0.30} Mg _{0.10}	1.99
Mn13	M7b	0.22309(5)	0.29804(7)	0.34013(3)	0.01247(13)	[25.0] Mn _{0.60} Fe _{0.40}	1.90
Al	Al	0.00363(11)	0.50120(15)	0.99823(7)	0.00546(17)	1	3.21
P1		0.11752(7)	0.99477(9)	0.86640(5)	0.00653(17)	1	4.77
P2		0.42104(7)	0.49673(10)	0.16091(5)	0.00998(19)	1	4.83
P3		0.13261(7)	0.54033(12)	0.92281(5)	0.00668(18)	1	4.77
P4		0.87365(7)	0.46858(11)	0.07432(5)	0.00595(18)	1	4.87
P5		0.12924(7)	0.25278(11)	0.03774(5)	0.0063(2)	1	4.80
P6		0.37905(7)	0.25198(11)	0.96040(5)	0.0060(2)	1	4.83
P7		0.10895(7)	0.76482(11)	0.04545(5)	0.00644(19)	1	4.80
P8		0.90048(7)	0.23202(11)	0.95247(5)	0.00591(19)	1	4.83
P9		0.87083(7)	0.27580(12)	0.78599(5)	0.0077(2)	1	4.83
P10		0.13229(7)	0.72527(12)	0.20905(5)	0.00690(19)	1	4.84
P11		0.85859(8)	0.70521(12)	0.79109(5)	0.0097(2)	1	4.85
P12		0.14301(8)	0.29528(12)	0.20257(5)	0.0090(2)	1	4.84
O1		0.4803(2)	0.5613(3)	0.13091(15)	0.0136(6)	1	1.90
O2		1.0295(2)	0.9407(3)	0.86616(14)	0.0105(6)	1	1.87
O3		0.3893(2)	0.3646(3)	0.13296(14)	0.0105(6)	1	1.99
O4		0.1140(2)	0.1472(3)	0.86031(14)	0.0110(6)	1	1.80
O5		0.6452(2)	0.4262(3)	0.81890(14)	0.0146(7)	1	1.92
O6		0.1826(2)	0.9606(3)	0.92221(13)	0.0131(6)	1	1.97
O7		0.4773(3)	0.4732(4)	0.22429(16)	0.0313(10)	OH	1.16
O8		0.3488(3)	0.5824(4)	0.1651(2)	0.0297(10)	1	1.87
O9		0.0509(2)	0.5586(3)	0.94200(13)	0.0078(5)	1	1.99
O10		0.95251(19)	0.4458(3)	0.05341(13)	0.0080(5)	1	1.99
O11		0.1263(2)	0.4060(3)	0.89316(14)	0.0113(6)	1	1.92
O12		0.8824(2)	0.5997(3)	0.10541(14)	0.0110(6)	1	1.93
O13		0.1288(2)	0.6612(3)	0.88252(14)	0.0112(6)	1	1.83
O14		0.3747(2)	0.8468(3)	0.11179(13)	0.0100(6)	1	1.97
O15		0.2119(2)	0.5599(4)	0.97063(14)	0.0141(6)	1	1.86
O16		0.2923(2)	0.9669(3)	0.02541(14)	0.0108(6)	1	1.95
O17		0.0849(2)	0.1664(3)	0.07187(14)	0.0123(6)	1	1.98
O18		0.4181(2)	0.3335(3)	0.92143(14)	0.0095(6)	1	2.00
O19		0.0989(2)	0.3975(3)	0.03522(13)	0.0091(6)	1	1.95
O20		0.90897(19)	0.6075(3)	0.96329(13)	0.0075(5)	1	1.97
O21		0.1116(2)	0.1916(3)	0.97755(14)	0.0128(6)	1	1.99
O22		0.4003(2)	0.3166(3)	1.01864(13)	0.0112(6)	1	1.96
O23		0.2248(2)	0.2470(3)	0.06207(15)	0.0135(7)	1	1.88
O24		0.2819(2)	0.2484(3)	0.93595(14)	0.0115(6)	1	1.94
O25		0.0528(2)	0.6420(3)	0.04699(13)	0.0081(6)	1	2.15
O26		0.9564(2)	0.3560(3)	0.95192(13)	0.0070(5)	1	2.11
O27		0.0745(2)	0.8701(3)	0.07879(13)	0.0102(6)	1	2.09
O28		0.9378(2)	0.1291(3)	0.91995(14)	0.0094(6)	1	2.07
O29		0.0971(2)	0.8141(3)	0.98479(13)	0.0106(6)	1	1.94
O30		0.9052(2)	0.1836(3)	1.01178(14)	0.0128(6)	O, OH	1.71
O31		0.2019(2)	0.7353(4)	0.07080(14)	0.0123(6)	1	1.75
O32		0.8096(2)	0.2666(3)	0.92154(15)	0.0132(6)	1	1.98
O33		0.9527(2)	0.3219(4)	0.82734(14)	0.0145(7)	1	1.93
O34		0.0505(2)	0.6792(3)	0.16745(13)	0.0117(6)	1	1.97
O35		0.8683(2)	0.6791(4)	0.22681(14)	0.0159(7)	1	1.94
O36		0.1381(2)	0.6721(4)	0.26732(14)	0.0157(7)	1	1.91

(Continued)

Table 4. (Continued.)

Site	Site2 ¹	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i>	s.o.f./site composition ²	BVS ³
O37		0.8621(3)	0.1233(4)	0.78913(16)	0.0228(8)	1	1.87
O38		0.1363(2)	0.8793(3)	0.20893(15)	0.0162(7)	1	1.87
O39		0.7967(2)	0.3383(4)	0.80454(15)	0.0155(7)	1	2.06
O40		0.2055(2)	0.6687(4)	0.18801(15)	0.0156(7)	1	2.01
O41		0.9456(2)	0.6661(4)	0.82875(15)	0.0159(7)	1	1.90
O42		0.0599(2)	0.3371(3)	0.16176(14)	0.0125(6)	1	1.94
O43		0.8481(3)	0.3492(5)	0.23286(17)	0.0396(14)	1	1.84
O44		0.1450(3)	0.3426(4)	0.26156(15)	0.0268(10)	1	1.90
O45		0.8525(2)	0.8585(3)	0.79108(15)	0.0138(7)	1	2.02
O46		0.1531(2)	0.1436(3)	0.20252(14)	0.0139(7)	1	2.01
O47		0.7882(2)	0.6482(4)	0.81551(18)	0.0230(8)	1	1.87
O48		0.2159(2)	0.3596(4)	0.18281(17)	0.0209(8)	1	1.91
O49		0.2352(2)	0.9957(4)	0.13510(17)	0.0190(8)	OH	0.97
O50		0.2727(2)	0.5013(3)	0.86372(15)	0.0116(6)	OH	0.97

¹According to the nomenclature by Chopin *et al.* (2006), the Ca site was renamed as C to handle homovalent substitutions at the site.

²Based on the *e_{ref}* values (given in square brackets) and electron microprobe data, taking also into account coordination polyhedra character, BVS and interatomic distances.

³BVS were calculated taking into account s.o.f. using bond-valence parameters of Brese and O'Keefe (1991).

Table 5. Selected interatomic distances (Å) in the structure of manganoarrodite-(KNa).

K-O35	2.693(4)	Fe1-O24	2.003(3)	Fe7-O42	2.062(3)	Mn11-O35	2.026(4)	P5-O17	1.528(3)
K-O36	2.760(4)	Fe1-O16	2.048(3)	Fe7-O1	2.079(4)	Mn11-O23	2.139(3)	P5-O23	1.531(4)
K-O34	2.850(4)	Fe1-O6	2.056(3)	Fe7-O14	2.127(3)	Mn11-O12	2.164(3)	P5-O19	1.533(3)
K-O44	2.873(4)	Fe1-O21	2.064(4)	Fe7-O30	2.135(3)	Mn11-O49	2.277(4)	P5-O21	1.557(3)
K-O43	2.908(5)	Fe1-O23	2.501(4)	Fe7-O17	2.145(3)	Mn11-O3	2.319(3)	<P5-O>	1.537
K-O33	2.919(4)	<Fe1-O>	2.134	Fe7-O10	2.211(3)	Mn11-O48	2.440(4)		
K-O41	3.031(4)			<Fe7-O>	2.127	<Mn11-O>	2.228	P6-O22	1.525(3)
K-O42	3.039(4)	Fe2-O45	2.070(3)					P6-O20	1.528(3)
<K-O>	2.884	Fe2-O48	2.081(4)	Fe8-O34	2.011(3)	Fe12-O43	2.079(4)	P6-O18	1.532(3)
		Fe2-O37	2.134(4)	Fe8-O22	2.062(3)	Fe12-O14	2.080(3)	P6-O24	1.553(4)
Na1-O28	2.349(4)	Fe2-O40	2.151(4)	Fe8-O12	2.121(3)	Fe12-O40	2.145(4)	<P6-O>	1.535
Na1-O27	2.378(4)	Fe2-O8	2.172(4)	Fe8-O3	2.151(3)	Fe12-O31	2.151(3)		
Na1-O29	2.482(4)	<Fe2-O>	2.122	Fe8-O27	2.264(3)	Fe12-O49	2.229(4)	P7-O31	1.522(3)
Na1-O30	2.561(5)			Fe8-O25	2.322(3)	Fe12-O8	2.311(4)	P7-O29	1.534(3)
Na1-O17	2.569(5)	Fe3-O38	2.074(3)	<Fe8-O>	2.155	<Fe12-O>	2.166	P7-O27	1.540(3)
Na1-O18	2.619(4)	Fe3-O5	2.076(3)					P7-O25	1.551(3)
Na1-O22	2.639(5)	Fe3-O39	2.109(4)	Fe9-O33	2.001(3)	Mn13-O44	2.059(4)	<P7-O>	1.537
Na1-O21	2.778(5)	Fe3-O46	2.121(3)	Fe9-O4	2.122(3)	Mn13-O13	2.139(3)		
<Na1-O>	2.547	Fe3-O47	2.137(4)	Fe9-O11	2.122(3)	Mn13-O39	2.170(4)	P8-O30	1.521(3)
		<Fe3-O>	2.103	Fe9-O21	2.127(3)	Mn13-O50	2.193(3)	P8-O32	1.528(4)
Na2-O26	2.358(4)			Fe9-O28	2.261(3)	Mn13-O32	2.217(3)	P8-O28	1.536(3)
Na2-O20	2.359(4)	Fe4-O27	2.017(3)	Fe9-O26	2.309(3)	Mn13-O5	2.575(4)	P8-O26	1.553(3)
Na2-O47	2.407(5)	Fe4-O46	2.033(3)	<Fe9-O>	2.157	<Mn13-O>	2.226	<P8-O>	1.535
Na2-O39	2.417(5)	Fe4-O49	2.050(4)						
Na2-O33	2.624(5)	Fe4-O17	2.168(3)	Fe10-O36	2.044(3)	P1-O5	1.532(3)	P9-O35	1.516(4)
Na2-O41	2.628(5)	Fe4-O38	2.181(4)	Fe10-O11	2.167(3)	P1-O6	1.535(3)	P9-O33	1.526(4)
Na2-O32	2.792(5)	Fe4-O1	2.201(3)	Fe10-O50	2.227(3)	P1-O4	1.537(3)	P9-O37	1.542(4)
<Na2-O>	2.512	<Fe4-O>	2.108	Fe10-O24	2.227(3)	P1-O2	1.551(3)	P9-O39	1.553(4)
				Fe10-O4	2.273(3)	<P1-O>	1.539	<P9-O>	1.534
				Fe10-O47	2.380(4)				
Na3-O15	2.231(4)	Fe5-O28	2.057(3)	<Fe10-O>	2.22	P2-O8	1.498(4)	P10-O36	1.509(3)
Na3-O22	2.369(4)	Fe5-O45	2.068(3)			P2-O3	1.521(3)	P10-O34	1.528(3)
Na3-O23	2.424(4)	Fe5-O50	2.090(4)			P2-O1	1.523(3)	P10-O38	1.548(4)
Na3-O3	2.486(4)	Fe5-O37	2.117(4)	Mn-O32	2.174(4)	P2-O7	1.601(4)	P10-O40	1.549(4)
<Na3-O>	2.378	Fe5-O18	2.169(3)	Mn-O6	2.242(3)	<P2-O>	1.536	<P10-O>	1.534
		Fe5-O2	2.211(3)	Mn-O16	2.244(3)				
Na4-O25	2.278(4)	<Fe5-O>	2.119	Mn-O29	2.269(4)				
Na4-O19	2.341(4)			Mn-O15	2.291(4)	P3-O15	1.517(3)	P11-O43	1.500(4)
Na4-O42	2.383(4)	Fe6-O41	2.053(4)	Mn-O31	2.495(4)	P3-O11	1.524(3)	P11-O41	1.534(4)
Na4-O48	2.405(4)	Fe6-O18	2.088(3)	<Mn-O>	2.286	P3-O13	1.558(3)	P11-O45	1.542(3)
Na4-O40	2.426(4)	Fe6-O2	2.098(3)			P3-O9	1.560(3)	P11-O47	1.557(4)
Na4-O34	2.502(4)	Fe6-O13	2.143(3)	Al-O9	1.858(3)	<P3-O>	1.540	<P11-O>	1.533
Na4-O10	2.910(4)	Fe6-O9	2.182(3)	Al-O10	1.870(3)				
<Na4-O>	2.464	Fe6-O29	2.203(3)	Al-O26	1.884(3)	P4-O12	1.510(3)	P12-O44	1.520(4)
		<Fe6-O>	2.128	Al-O25	1.888(3)	P4-O14	1.529(3)	P12-O42	1.522(4)
				Al-O20	1.895(3)	P4-O16	1.541(3)	P12-O46	1.532(4)
Na5-O5	2.325(5)			Al-O19	1.900(4)	P4-O10	1.545(3)	P12-O48	1.558(4)
Na5-O7	2.406(5)			<Al-O>	1.883	<P4-O>	1.531	<P12-O>	1.533
Na5-O2	2.616(4)								
Na5-O41	2.631(5)								
Na5-O44	2.659(6)								
<Na5-O>	2.527								

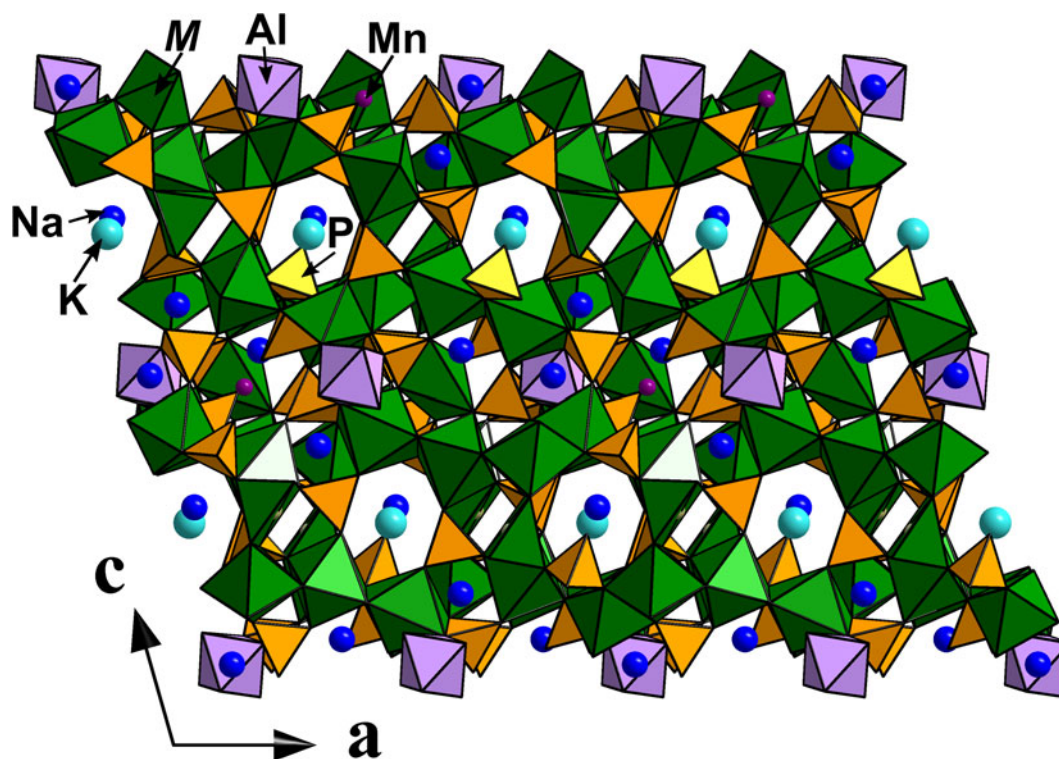


Fig. 4. General view of the crystal structure of manganarrojadite-(KNa). Projection on (010).

Table 6. Assignment of cation sites for minerals of the arrojadite group (compiled after Chopin et al., 2006, with additions)*.

Sites**	A1	A2	B1	B1b,c	B2	C	Na1	Na2	Na3	Al	M	P	W	Ref
Arrojadite-(KNa)	K	Na	Na		Na	Ca	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	(OH) ₂	1
Arrojadite-(KFe)	K	Na		Fe	□	Ca	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	(OH) ₂	1
Arrojadite-(BaFe)	Ba	□		Fe	□	Ca	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	(OH) ₂	1
Arrojadite-(SrFe)	Sr	□		Fe	□	Ca	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	(OH) ₂	1
Arrojadite-(PbFe)	Pb	□		Fe	□	Ca	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	(OH) ₂	1
Dickinsonite-(KMnNa)	K	Na		Mn	□	Ca	Na	Na	Na	Al	Mn ₁₃	(PO ₄) ₁₁ PO ₄	(OH) ₂	1
Fluorarrojadite-(BaNa)	Ba	□	Na		Na	Ca	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	F ₂	1,2
Fluorarrojadite-(BaFe)	Ba	□		Fe	□	Ca	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	F ₂	1
Fluorcarmoite-(BaNa)	Ba	□	Na		Na	Ca	Na	Na	□	Al	Mg ₁₃	(PO ₄) ₁₁ PO ₃ OH	F ₂	3
Manganarrojadite-(KNa)	K	Na	Na		Na	Mn	Na	Na	□	Al	Fe ₁₃	(PO ₄) ₁₁ PO ₃ OH	(OH) ₂	4

*Does not include arrojadite-(BaNa) as its structure was reported in the *C2/c* space group (Vignola et al., 2016) and it is difficult to compare its cation distribution with the nomenclature scheme established by Cámara et al. (2006) and Chopin et al. (2006).

References: [1] Chopin et al. (2006); [2] Števkó et al. (2018); [3] Cámara et al. (2019); [4] this work.

**The general structural formula for arrojadite-group minerals is $A_2B_2CNa_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$ (after Cámara et al., 2006; with the Ca site labelled as C to handle homovalent substitutions at the site).

□ = vacancy.

indicate that the dominant cation at the Mn site is Mn^{2+} and not Fe^{2+} . If the Mn site were occupied by Fe atoms, the BVS would be unjustifiably low (1.62 vu).

The BVS at the O7 [1.16 vu], O49 [0.97 vu] and O50 [0.97 vu] sites show that they are occupied by hydroxyl groups, while the O30 and, possibly, O31 sites have mixed O/OH occupancies [1.71 and 1.75 vu, respectively] with a predominant O^{2-} anion (Table 4). A similar partial protonation of an oxygen in one of the PO_4 groups was observed in the recently described arrojadite-group mineral fluorcarmoite-(BaNa) $BaNa_4CaMg_{13}Al(PO_4)_{11}(PO_3OH)F_2$ (site O4a, 1.63 vu; Cámara et al., 2019). The presence of hydroxyl groups at the O7, O30 and O31 sites means that PO_3OH groups are present. The remaining 45 anion sites are occupied by O atoms. The bands at 3532 and 3557 cm^{-1} in the

IR spectra of manganarrojadite-(KNa) confirm the presence of hydroxyl groups (Fig. 3). Both BVS and IR data indicate the absence of H_2O^0 .

Discussion

The resulting structural formula of manganarrojadite-(KNa) $K_{0.88}Na_{4.75}(Mn_{0.88}Ca_{0.12})_{\Sigma 1.00}(Fe_{9.10}Mn_{2.80}Mg_{1.10})_{\Sigma 13.00}Al_{1.00}(PO_4)_{10.62}(PO_3OH)_{1.38}(OH)_{2.00}$ is in good agreement with the empirical formula $K_{0.80}Na_{4.73}(Mn_{0.91}Ca_{0.12})_{\Sigma 1.03}(Fe_{9.13}Mn_{2.74}Mg_{1.13})_{\Sigma 13.00}Al_{1.00}(PO_4)_{10.59}(PO_3OH)_{1.41}(OH)_{1.67}F_{0.33}\Sigma 22.00$. Combining our data with the nomenclature scheme established by Chopin et al. (2006) leads to the ideal structural formula

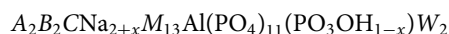
Table 7. Comparative data for manganarrojadite-(KNa) and selected arrojadite-group minerals.

Mineral	Manganarrojadite-(KNa)	Arrojadite-(KNa)	Arrojadite-(BaNa)
Formula	$\text{KNa}_5\text{Mn}^{2+}\text{Fe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$	$\text{KNa}_5\text{CaFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$	$\text{BaNa}_3(\text{NaCa})\text{Fe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	Cc	Cc	C2/c
<i>a</i> (Å)	16.5345(3)	16.5220(11)	16.4984(6)
<i>b</i> (Å)	10.0406(2)	10.0529(7)	10.0228(3)
<i>c</i> (Å)	24.6261(5)	24.6477(16)	24.648(1)
β (°)	105.891(2)	106.509(2)	105.850(4)
<i>V</i> (Å ³)	3932.09(14)	3932.2(7)	3920.8(2)
<i>Z</i>	4	4	4
<i>D</i> , g/cm ³	3.53 (calc)	3.44 (calc)	3.54 (meas)
Strongest reflections of the powder XRD pattern: <i>d</i> , Å (<i>I</i>)	5.902 (24) 5.025 (24) 3.208 (47) 3.048 (100) 2.758 (24) 2.704 (70)	5.861 (29) 5.026 (27) 3.186 (33) 3.050 (100) 2.798 (25) 2.793 (28) 2.691 (71)	3.388 (28) 3.203 (46) 3.037 (100) 2.778 (32) 2.718 (61) 2.567 (35)
References	This work	Cámara <i>et al.</i> (2006); Chopin <i>et al.</i> (2006)	Vignola <i>et al.</i> (2016)

$A^1K^{A2}Na^{B1}Na^{B2}Na^{Na1,2}Na_2Na_3\Box^C Mn^M Fe_{13}Al(PO_4)_{11}(PO_3OH)W(OH)_2$ (the Ca site labelled as C; Tables 4, 6).

Manganarrojadite-(KNa) is a Mn^{2+} dominant analogue [with $Mn^{2+} > Ca$ at the C site] of arrojadite-(KNa), ideally $\text{KNa}_5\text{CaFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$ (Cámara *et al.*, 2006; Chopin *et al.*, 2006; Tables 6, 7). It is the first arrojadite group with a dominant bivalent cation (Mn^{2+}) other than Ca at the C site (Table 6), without Ca as the dominant cation at any cation site in the structure and with such a low Ca content (0.82 wt.% CaO, 0.12 apfu Ca) in general. An arrojadite-group mineral from Sidi-bou-Kricha, Morocco with a low Ca content (0.32 apfu) was mentioned by Huvelin *et al.* (1972) and, as suggested by Chopin *et al.* (2006), could be due to Ba atoms occupying the C site resulting in 'fluorbarioarrojadite-(NaFe)'. However, a phase with such composition has never been studied in detail. Moreover, all analyses of arrojadite-group minerals from Sidi-bou-Kricha obtained by Chopin *et al.* (2006) show CaO contents in the range 2.2–2.4 wt.%; thus, the low Ca value in the original analysis might have been an error. Arrojadite-(BaNa) is the only other arrojadite-group mineral with significant differences in the occupancy of the C site (Vignola *et al.*, 2016; Tables 6, 7). Its structure was reported in the C2/c space group, and so it is difficult to compare it with other arrojadite-group minerals reported in the Cc space group; nevertheless, the site generally populated by Ca atoms in arrojadite-group minerals hosts Na atoms in arrojadite-(BaNa) and the M(1) site, dominated by Fe atoms in arrojadite-group minerals, is occupied by Ca atoms in arrojadite-(BaNa).

We propose revising the currently used general structural formula for the arrojadite group $A_2B_2CaNa_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$ (Cámara *et al.*, 2006) as:



where C = Ca, Mn^{2+} to handle homovalent substitutions at the C site.

The existing criteria for arrojadite-group nomenclature are based on the assumption that the C site is always occupied by Ca and/or larger bivalent cations (Sr, Ba), and thus it is postulated that when calculating chemical analyses for classification purposes the C site is filled with Ca and A^{2+} cations of increasing radius before bivalent cations are assigned to the A1 site (Chopin *et al.*, 2006). The discovery of manganarrojadite-(KNa) indicates that

the C site can be occupied by smaller bivalent cations as well. The available data are not sufficient to analyse the implications of this fact, but it shows that a systematic structural study of arrojadite-group minerals is required to fully understand the distribution of Ca between various sites in the arrojadite type structure.

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