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

Inna Lykova^{1*}, Ralph Rowe¹, Glenn Poirier¹, Kate Helwig², Henrik Friis³

¹Canadian Museum of Nature, PO Box 3443, Station "D", Ottawa, Ontario K1P 6P4, Canada

²Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario K1B 4S7, Canada

³Natural History Museum, University of Oslo, PO Box 1172, Blindern, Oslo N-0318, Norway

*e-mail: ilykova@nature.ca

Short Title: Manganoarrojadite-(KNa), a new mineral

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 x 1.5 cm in size combined in aggregates with vivianite, goyazite, quartz and calcite. The mineral is olive green with pale green streak and vitreous to greasy lustre. The cleavage is good in one direction. The Mohs hardness is 4½. D_{calc} is 3.53 g/cm³. Manganoarrojadite-(KNa) is optically biaxial (–), $\alpha = 1.658(2)$, $\beta = 1.666(2)$, $\gamma = 1.670(2)$, 2V (meas.) = 67(1)°, 2V (calc.) = 70° (589 nm). The IR spectrum is reported. The composition (wt.%) is Na₂O 6.97, K₂O 1.78, CaO 0.31, MgO 2.17, MnO 12.30, FeO 31.17, Al₂O₃ 2.43, P₂O₅ 40.48, F 0.30, H₂O 1.32, O = F₂ -0.13, total 99.10. The empirical formula calculated on the basis of 12 P and (O+OH+F) = 50 *apfu* is Na_{4.73}K_{0.80}Ca_{0.12}Mg_{1.13}Mn²⁺_{3.65}Fe²⁺_{9.13}Al_{1.00}P_{12.00}O_{46.59}OH_{3.08}F_{0.33}. The ideal structural formula is ^{A1}K^{A2}Na^{B1}Na^{B2}Na^{Na1,2}Na^{Na3}□^CMn^MFe₁₃Al(PO₄)₁₁(PO₃OH)^W(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

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$Z = 4$. The strongest reflections of the powder X-ray diffraction pattern [$d, \text{\AA}(hkl)$] 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)($\bar{6}02$), 2.704(70)(226). The crystal structure, refined from single-crystal X-ray diffraction data ($R_1 = 0.025$), is of the arrojadite 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

Introduction

Arrojadite-group minerals are complex primary pegmatite phosphates with the general structural formula $A_2B_2CNa_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$ (after Cámara *et al.*, 2006; with the Ca site labelled as C). Eleven members of the group are currently known [IMA-CNMNC List of Mineral Names (September 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; Fe²⁺ – arrojadite, Mn²⁺ – 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 Fe³⁺ over Al at the *A1* site [*e.g.* fluorarrojadite-(BaFe)]. The nomenclature also proposed handling potential monovalent substitutions at the *C* site in the same way as for the *A1* site, *i.e.* by using an appropriate prefix like bario- or strontio-.

Manganoarrojadite-(KNa), ideally $KNa_5MnFe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$, 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 Fe²⁺ 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 Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, proposal IMA 2020-003. The specimen CMNMC 47194 became the holotype of manganoarrojadite-(KNa).

Occurrence and general appearance

Manganoarrojadite-(KNa) occurs at the Palermo No. 1 mine, Grafton Co., New Hampshire, USA. The mine exploited a large phosphate bearing granite pegmatite 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 x 1.5 cm in size (Fig. 1) combined in aggregates. Manganoarrojadite-(KNa) was partially replaced along intergrain fractures by vivianite $\text{Fe}^{2+}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (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 manganoarrojadite-(KNa) is olive green with 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 XRD data is 3.53 g/cm³.

Manganoarrojadite-(KNa) is optically biaxial (–), $\alpha = 1.658(2)$, $\beta = 1.666(2)$, $\gamma = 1.670(2)$, 2V (meas.) = 67(1)° (from a spindle-stage extinction curve); 2V (calc.) = 70° (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 manganoarrojadite-(KNa) were obtained using a JEOL 8230 SuperProbe electron microscope equipped with five WDS 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 $KK\alpha$, $NaK\alpha$, $FeK\alpha$, $FK\alpha$ and $PK\alpha$.

The Fourier transform infrared (FTIR) spectrum of manganoarrojadite-(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 manganoarrojadite-(KNa) was mounted on a low-pressure 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 X-ray diffraction 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 $\text{I}\mu\text{S}$ 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 fiber pin mount, was analysed with continuous Φ rotation and 10° rocking motion along the Ψ 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 manganoarrojadite-(KNa) are given in Table 1. The data based on 11 analyses of four crystal fragments from 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 $(\text{O}+\text{OH}+\text{F}) = 50 \text{ apfu}$ is $\text{Na}_{4.73}\text{K}_{0.80}\text{Ca}_{0.12}\text{Mg}_{1.13}\text{Mn}^{2+}_{3.65}\text{Fe}^{2+}_{9.13}\text{Al}_{1.00}\text{P}_{12.00}\text{O}_{46.59}\text{OH}_{3.08}\text{F}_{0.33}$. 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 X-ray diffraction 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 X-ray diffraction 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 $R1 = 0.025$ 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. Crystallographic information file (CIF) for manganoarrojadite-(KNa) is available as a Supplementary file. It was also 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 $\langle M-O \rangle$ distances of 2.220, 2.228, and 2.226 Å, respectively, and thus characterized 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 thirteen 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 the 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 $\langle \text{Mn}-\text{O} \rangle$ 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 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 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) $\text{BaNa}_4\text{CaMg}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})\text{F}_2$ (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 manganoarrojadite-(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 manganoarrojadite-(KNa) $\text{K}_{0.88}\text{Na}_{4.73}(\text{Mn}^{2+}_{0.88}\text{Ca}_{0.12})_{\Sigma 1.00}(\text{Fe}^{2+}_{9.10}\text{Mn}^{2+}_{2.80}\text{Mg}_{1.10})_{\Sigma 13.00}\text{Al}_{1.00}(\text{PO}_4)_{10.62}(\text{PO}_3\text{OH})_{1.38}(\text{OH})_{2.00}$ is in good agreement with the empirical formula $\text{K}_{0.80}\text{Na}_{4.73}(\text{Mn}^{2+}_{0.91}\text{Ca}_{0.12})_{\Sigma 1.03}(\text{Fe}^{2+}_{9.13}\text{Mn}^{2+}_{2.74}\text{Mg}_{1.13})_{\Sigma 13.00}\text{Al}_{1.00}(\text{PO}_4)_{10.59}(\text{PO}_3\text{OH})_{1.41}(\text{OH})_{1.67}\text{F}_{0.33}$ $\Sigma 2.00$.

Combining our data with the nomenclature scheme established by Chopin *et al.* (2006) leads to the ideal structural formula $^{A1}\text{K}^{A2}\text{Na}^{B1}\text{Na}^{B2}\text{Na}^{\text{Na}1,2}\text{Na}_2^{\text{Na}3}\square^{\text{C}}\text{Mn}^{\text{M}}\text{Fe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})^{\text{W}}(\text{OH})_2$ (the Ca site labelled as C; Tables 4, 6).

Manganoarrojadite-(KNa) is a Mn^{2+} dominant analogue [with $\text{Mn}^{2+} > \text{Ca}$ 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 $\text{C}2/c$ 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 $\text{A}_2\text{B}_2\text{CaNa}_{2+x}\text{M}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH}_{1-x})\text{W}_2$ (Cámara *et al.*, 2006) as

$A_2B_2CNa_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$ 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 postulate 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 manganoarrojadite-(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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Figure captions

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

Fig. 2. Manganarrojadite-(KNa) partially replaced by vivianite. Polished section. SEM (BSE) image.

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

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

Table 1. Chemical data (in wt %, average of 11 analyses) for manganoarrojadite-(KNa).

Constituent	Mean	Range	Stand. Dev.
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.

Table 2. X-ray powder-diffraction data of manganoarrojadite-(KNa).

<i>I</i> _{obs.}	<i>I</i> _{calc.} ¹	<i>d</i> _{obs.}	<i>d</i> _{calc.} ²	<i>hkl</i>
6	8	11.87	11.87	002
6	7	8.50	8.50	110
6	5	7.95	7.97	200
17	17	7.66	7.67	$\bar{2}02$
6	4	7.45	7.45	$\bar{1}12$
15	15	6.47	6.48	112
12	9	5.932	5.935	004
24	23	5.902	5.903	202
14	18	5.546	5.549	$\bar{2}04$
4	2	5.248	5.243	$\bar{1}14$
24	27	5.025	5.027	020
4	3	4.784	4.784	$\bar{3}12$
4	3	4.693	4.675	310
8	8	4.629	4.629	022
13	10	4.559	4.561	114
6	5	4.135	4.135	$\bar{4}02$
5	2	3.981	3.983	400
6	3	3.471	3.472	$\bar{3}16$
5	3	3.450	3.452	025

21	20	3.401	3.401	116
13	11	3.308	3.310	314
5	5	3.281	3.279	130
5	4	3.237	3.237	224
47	33, 17	3.208	3.208, 3.208	206, 132
8	5	3.138	3.137	317
7	2, 4	3.118	3.118, 3.116	511, 132
100	8, 100	3.048	3.048, 3.048	514, 424
5	2, 3	2.938	2.940, 2.933	118, 515
5	4	2.871	2.870	422
20	21	2.853	2.853	332
12	9, 9	2.839	2.841, 2.834	318, 330
13	11	2.804	2.804	134
18	18	2.790	2.790	516
20	19	2.775	2.775	408
24	22	2.758	2.758	602
10	3, 3	2.717	2.718, 2.716	334, 316
70	81	2.704	2.704	226
7	5	2.669	2.669	332
9	9	2.600	2.599	136
15	9, 6	2.556	2.556, 2.555	028, 606
20	20	2.545	2.545	424
16	19	2.513	2.513	040
4	3	2.470	2.469	2.0.10
13	14	2.429	2.429	428
13	13	2.418	2.418	622
8	7	2.392	2.392	624
4	2	2.344	2.344	625
3	2	2.317	2.314	044
7	5	2.309	2.309	530
5	2	2.272	2.271	318
5	5	2.264	2.262	535
6	4	2.222	2.221	045
10	8	2.206	2.206	716
5	3	2.147	2.147	0.2.10
5	2	2.123	2.122	046
7	3, 2, 2	2.117	2.120, 2.116, 2.116	2.0.10, 408, 537
3	3	2.103	2.102	444
5	4	1.9917	1.9912	800
7	4	1.9785	1.9785	152
9	7, 6	1.9515	1.9538, 1.9503	2.2.10, 428
4	3	1.9453	1.9453	248
11	2, 8, 2, 3	1.9165	1.9179, 1.9162, 1.9135, 1.9135	048, 808, 444, 338

5	3, 3	1.8832	1.8859, 1.8826	$\bar{3}52, 730$
3	3	1.8630	1.8628	$\bar{4}48$
5	3, 2	1.8578	1.8577, 1.8537	$\bar{6}42, \bar{3}.3.11$
4	3, 2, 3	1.7903	1.7969, 1.7905,	$732, \bar{8}28, \bar{8}.0.10$
13	10, 7	1.7616	1.7615, 1.7605	$\bar{2}.4.10, \bar{2}.0.14$
11	2, 11	1.7550	1.7570, 1.7547	156, 642
5	3, 3	1.7472	1.7478, 1.7475	804, $\bar{3}.3.12$
2	3	1.7371	1.7360	$\bar{6}.2.12$
3	4	1.7143	1.7140	$\bar{4}.4.10$
3	2	1.7010	1.7004	550
6	6	1.6831	1.6827	$\bar{1}58$
5	2, 5, 4	1.6615	1.6636, 1.6616, 1.6591	$\bar{3}58, \bar{2}.2.14, 062$
10	3, 3, 7	1.6513	1.6531, 1.6529, 1.6509	$\bar{5}56, 1.3.12, 824$
7	7	1.6043	1.6041	4.0.12
9	6, 3	1.5678	1.5677, 1.5672	$6.0.10, \bar{8}.2.12$
5	4	1.5616	1.5618	$\bar{1}0.2.6$
4	4	1.5355	1.5353	$\bar{4}64$
6	3	1.5281	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, $\beta = 106.0253(7)^\circ$, $V = 3955.60(7)$ Å³.

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)	$0.019 \times 0.040 \times 0.058$
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)	MoK α , 0.71073
Number of frames	1327
θ range (°)	2.40 – 33.39
Absorption correction	CrysAlisPro (Rigaku Oxford Diffraction, 2019)
$T_{\min}$, $T_{\max}$	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° θ (%)	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 [$I > 2\sigma I$], $R_1(\text{all})$	0.025, 0.027
wR_2 [$I > 2\sigma I$], $wR_2(\text{all})$	0.065, 0.066
GoF	1.029
No. of refined parameters	751
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e $^{-}$ Å $^{-3}$)	1.88 / -0.88

Table 4. Coordinates and equivalent displacement parameters (U_{eq} in $\text{\AA}^2$) of atoms, site occupancy factors (s.o.f.), and bond-valence sums for manganoarrojadite-(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)	1.01474(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

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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
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'Keeffe (1991).

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

K–O35	2.693(4)	Na4–O25	2.278(4)	Fe2–O45	2.070(3)	Fe7–O42	2.062(3)	Mn11–O35	2.026(4)
K–O36	2.760(4)	Na4–O19	2.341(4)	Fe2–O48	2.081(4)	Fe7–O1	2.079(4)	Mn11–O23	2.139(3)
K–O34	2.850(4)	Na4–O42	2.383(4)	Fe2–O37	2.134(4)	Fe7–O14	2.127(3)	Mn11–O12	2.164(3)
K–O44	2.873(4)	Na4–O48	2.405(4)	Fe2–O40	2.151(4)	Fe7–O30	2.135(3)	Mn11–O49	2.277(4)

K–O43	2.908(5)	Na4–O40	2.426(4)	Fe2–O8	2.172(4)	Fe7–O17	2.145(3)	Mn11–O3	2.319(3)
K–O33	2.919(4)	Na4–O34	2.502(4)	<Fe2–O>	2.122	Fe7–O10	2.211(3)	Mn11–O48	2.440(4)
K–O41	3.031(4)	Na4–O10	2.910(4)			<Fe7–O>	2.127	<Mn11–O>	2.228
K–O42	3.039(4)	<Na4–O>	2.464	Fe3–O38	2.074(3)				
<K–O>	2.884			Fe3–O5	2.076(3)	Fe8–O34	2.011(3)	Fe12–O43	2.079(4)
		Na5–O5	2.325(5)	Fe3–O39	2.109(4)	Fe8–O22	2.062(3)	Fe12–O14	2.080(3)
Na1–O28	2.349(4)	Na5–O7	2.406(5)	Fe3–O46	2.121(3)	Fe8–O12	2.121(3)	Fe12–O40	2.145(4)
Na1–O27	2.378(4)	Na5–O2	2.616(4)	Fe3–O47	2.137(4)	Fe8–O3	2.151(3)	Fe12–O31	2.151(3)
Na1–O29	2.482(4)	Na5–O41	2.631(5)	<Fe3–O>	2.103	Fe8–O27	2.264(3)	Fe12–O49	2.229(4)
Na1–O30	2.561(5)	Na5–O44	2.659(6)			Fe8–O25	2.322(3)	Fe12–O8	2.311(4)
Na1–O17	2.569(5)	<Na5–O>	2.527	Fe4–O27	2.017(3)	<Fe8–O>	2.155	<Fe12–O>	2.166
Na1–O18	2.619(4)			Fe4–O46	2.033(3)				
Na1–O22	2.639(5)	Mn–O32	2.174(4)	Fe4–O49	2.050(4)	Fe9–O33	2.001(3)	Mn13–O44	2.059(4)
Na1–O21	2.778(5)	Mn–O6	2.242(3)	Fe4–O17	2.168(3)	Fe9–O4	2.122(3)	Mn13–O13	2.139(3)
<Na1–O>	2.547	Mn–O16	2.244(3)	Fe4–O38	2.181(4)	Fe9–O11	2.122(3)	Mn13–O39	2.170(4)
		Mn–O29	2.269(4)	Fe4–O1	2.201(3)	Fe9–O21	2.127(3)	Mn13–O50	2.193(3)
Na2–O26	2.358(4)	Mn–O15	2.291(4)	<Fe4–O>	2.108	Fe9–O28	2.261(3)	Mn13–O32	2.217(3)
Na2–O20	2.359(4)	Mn–O31	2.495(4)			Fe9–O26	2.309(3)	Mn13–O5	2.575(4)
Na2–O47	2.407(5)	<Mn–O>	2.286	Fe5–O28	2.057(3)	<Fe9–O>	2.157	<Mn13–O>	2.226
Na2–O39	2.417(5)			Fe5–O45	2.068(3)				
Na2–O33	2.624(5)	Fe1–O24	2.003(3)	Fe5–O50	2.090(4)	Fe10–O36	2.044(3)	Al–O9	1.858(3)
Na2–O41	2.628(5)	Fe1–O16	2.048(3)	Fe5–O37	2.117(4)	Fe10–O11	2.167(3)	Al–O10	1.870(3)
Na2–O32	2.792(5)	Fe1–O6	2.056(3)	Fe5–O18	2.169(3)	Fe10–O50	2.227(3)	Al–O26	1.884(3)
<Na2–O>	2.512	Fe1–O21	2.064(4)	Fe5–O2	2.211(3)	Fe10–O24	2.227(3)	Al–O25	1.888(3)
		Fe1–O23	2.501(4)	<Fe5–O>	2.119	Fe10–O4	2.273(3)	Al–O20	1.895(3)
Na3–O15	2.231(4)	<Fe1–O>	2.134			Fe10–O47	2.380(4)	Al–O19	1.900(4)
Na3–O22	2.369(4)			Fe6–O41	2.053(4)	<Fe10–O>	2.22	<Al–O>	1.883
Na3–O23	2.424(4)			Fe6–O18	2.088(3)				
Na3–O3	2.486(4)			Fe6–O2	2.098(3)				

<Na3–O>	2.378	Fe6–O13	2.143(3)
		Fe6–O9	2.182(3)
		Fe6–O29	2.203(3)
		<Fe6–O>	2.128

Table 5.—*Extended*

P1–O5	1.532(3)	P5–O17	1.528(3)	P9–O35	1.516(4)
P1–O6	1.535(3)	P5–O23	1.531(4)	P9–O33	1.526(4)
P1–O4	1.537(3)	P5–O19	1.533(3)	P9–O37	1.542(4)
P1–O2	1.551(3)	P5–O21	1.557(3)	P9–O39	1.553(4)
<P1–O>	1.539	<P5–O>	1.537	<P9–O>	1.534
P2–O8	1.498(4)	P6–O22	1.525(3)	P10–O36	1.509(3)
P2–O3	1.521(3)	P6–O20	1.528(3)	P10–O34	1.528(3)
P2–O1	1.523(3)	P6–O18	1.532(3)	P10–O38	1.548(4)
P2–O7	1.601(4)	P6–O24	1.553(4)	P10–O40	1.549(4)
<P2–O>	1.536	<P6–O>	1.535	<P10–O>	1.534
P3–O15	1.517(3)	P7–O31	1.522(3)	P11–O43	1.500(4)
P3–O11	1.524(3)	P7–O29	1.534(3)	P11–O41	1.534(4)
P3–O13	1.558(3)	P7–O27	1.540(3)	P11–O45	1.542(3)
P3–O9	1.560(3)	P7–O25	1.551(3)	P11–O47	1.557(4)
<P3–O>	1.540	<P7–O>	1.537	<P11–O>	1.533
P4–O12	1.510(3)	P8–O30	1.521(3)	P12–O44	1.520(4)
P4–O14	1.529(3)	P8–O32	1.528(4)	P12–O42	1.522(4)
P4–O16	1.541(3)	P8–O28	1.536(3)	P12–O46	1.532(4)
P4–O10	1.545(3)	P8–O26	1.553(3)	P12–O48	1.558(4)

<P(4)–O>	1.531	<P8–O>	1.535	<P12–O>	1.533
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Table 6. Assignment of cation sites for minerals of the arrojadite group (compiled after Chopin *et al.*, 2006, with additions)*.

Sites**	A(1)	A(2)	B(1)	B(1b,c)	B(2)	C	Na(1)	Na(2)	Na(3)	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
Manganoarrojadite-(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).

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

Mineral	Manganoarrojadite-(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	<i>Cc</i>	<i>Cc</i>	<i>C2/c</i>
<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	5.902 (24)	5.861 (29)	3.388 (28)
reflections of	5.025 (24)	5.026 (27)	3.203 (46)
the powder X-	3.208 (47)	3.186 (33)	3.037 (100)
ray diffraction	3.048 (100)	3.050 (100)	2.778 (32)
pattern:	2.758 (24)	2.798 (25)	2.718 (61)
<i>d</i> , Å (<i>I</i>)	2.704 (70)	2.793 (28)	2.567 (35)
		2.691 (71)	
References	This work	Cámara <i>et al.</i> (2006); Chopin <i>et al.</i> (2006).	Vignola <i>et al.</i> (2016)