

The arrojadite-dickinsonite series, $\text{KNa}_4\text{Ca}(\text{Fe},\text{Mn})_{14}^{2+}\text{Al}(\text{OH})_2(\text{PO}_4)_{12}$: crystal structure and crystal chemistry

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Abstract

The complex crystal structure of the arrojadite-dickinsonite, $\text{KNa}_4\text{Ca}(\text{Fe},\text{Mn})_{14}^{2+}\text{Al}(\text{OH},\text{F})_2(\text{PO}_4)_{12}$, series was studied by single-crystal X-ray diffraction techniques. Three compositions were studied and one, dickinsonite from Branchville, Connecticut, is summarized here. The others are arrojadites from the Nancy Mine, North Groton, New Hampshire, and the Nickel Plate Mine, Keystone, South Dakota. Dickinsonite is monoclinic, $a = 24.940(6)$, $b = 10.131(4)$, $c = 16.722(2)\text{Å}$, $\beta = 105.60(2)^\circ$, space group $A2/a$, $Z = 4$. $R = 0.078$ for 7740 measured intensities. Of the 49 nonequivalent atoms in the asymmetric unit, fifteen are larger cations, whose coordination polyhedra include six symmetry-independent octahedra, one tetrahedron, one square pyramid, one seven-coordinated polyhedron, two distorted cubes, one non-cubic polyhedron of order eight, two of ten, and one of twelve-coordination.

The arrojadite-dickinsonite structure type is related to that of wylieite, $\text{Na}_2\text{Fe}_2^+\text{Al}(\text{PO}_4)_3$, as seen from a cell with $x_2 = 1/4 - x_1 + z_1$, $y_2 = 1/4 + y_1$, $z_2 = -x_1$, projected down z_2 , where (x_1, y_1, z_1) are parameters for the reduced cell used in the refinement. Eliminating disordered Ca in dickinsonite gives the same ratio $\sum(\text{M}+\text{X}) : \sum(\text{P}) = 5:3$ as for wylieite. Average bond distances in dickinsonite are

$^{14}\text{M}(1)\text{-O } 2.092$,	$^{15}\text{M}(2)\text{-O } 2.133$,	$^{16}\text{M}(3)\text{-O } 2.156$,	$^{16}\text{M}(4)\text{-O } 2.167$,
$^{16}\text{M}(5)\text{-O } 2.166$,	$^{16}\text{M}(6)\text{-O } 2.235$,	$^{15}\text{M}(7)\text{-O } 2.190$,	$^{16}\text{Al-O } 1.884$,
$^{18}\text{X}(1)\text{-O } 2.516$,	$^{17}\text{X}(2)\text{-O } 2.515$,	$^{18}\text{X}(3)\text{-O } 2.574$,	$^{110}\text{X}(4)\text{-O } 3.012$,
$^{18}\text{X}(5)\text{-O } 2.928$,	$^{110}\text{X}(6)\text{-O } 2.940$,	$^{112}\text{X}(7)\text{-O } 3.080 \text{ Å}$	

The sites M(1), X(1), X(4), X(6), and X(7) are disordered. In addition, one of the six non-equivalent (PO_4) tetrahedra is disordered, with evidence of splitting into a reciprocally coupled P(lx) site, which appears to be directly coupled with the X(6) population.

Introduction

Arrojadite and its isotype dickinsonite are complex primary alkali transition metal phosphates, which

have experienced a tumultuous investigative history. *Arrojadite* was originally named by Guimarães (1942) for material from the Serra Branca pegmatite,

Table 7. Arrojadite-dickinsonite: some characteristics of the nonequivalent cations*

Atom	KPPB	ERN	CN	NM	Occupancy			Next larger in crystal BR
					NP	BR	BR	
*† M(1)	X(7)	8	4	0.622(4) Fe ²⁺ + 0.378□	0.05 Li + 0.18 Mg + 0.50 Fe + 0.28□	0.46(1) Fe ²⁺ + 0.54□	2.509	0(12)
M(2)	X(5)	8	5	1.0 Fe ²⁺	1.0 Fe	1.0 Mn ²⁺	3.017	0(22)
M(3)	X(6)	8	6	0.519(7) Mn ²⁺ + 0.481 Mg ²⁺	1.0 Fe	0.5 Mn ²⁺ + 0.5 Fe ²⁺	3.195	M(4)
M(4)	X(2)	8	6	1.00 Fe ²⁺	1.0 Fe	0.5 Mn ²⁺ + 0.5 Fe ²⁺	3.097	0(10)
M(5)	X(1)	8	6	1.00 Fe ²⁺	1.0 Fe	0.5 Mn ²⁺ + 0.5 Fe ²⁺	3.206	0(5)
M(6)	X(3)	8	6	1.00 Fe ²⁺	1.0 Mn	0.92(1) Mn ²⁺ + 0.08 Mg ²⁺	3.165	0(23)
M(7)	X(4)	8	5(6)	0.5 Fe ²⁺ + 0.5 Mn ²⁺	1.0 Mn	0.93(1) Mn ²⁺ + 0.07 Na ¹⁺	2.543	0(3)
Al	X(8)	4	6	1.0 Al ³⁺	1.0 Al	0.84 Al ³⁺ + 0.16 Fe ³⁺	3.184	X(2)
* X(1)	--	8	8	0.38(1) Ca ²⁺ + 0.12 Mn ²⁺ + 0.50□	0.5 Ca + 0.5□	0.5 Ca ²⁺ + 0.5□	2.975	X(6)
X(2)	A(3)	8	7(8)	1.0 Na ¹⁺	1.0 Na	1.0 Na ¹⁺	3.032	0(5)
X(3)	A(2)	4	8	1.0 Na ¹⁺	1.0 Na	1.0 Na ¹⁺	3.506	0(1)
* X(4)	--	4	10	0.66(2) Na ¹⁺ + 0.34□	0.56 Na + 0.44□	0.49(1) K ¹⁺ + 0.51□	3.957	0(7)
X(5)	A(1)	4	8	0.972(2) K ¹⁺ + 0.028 Pb ²⁺	0.75 K + 0.25 Na	0.71(3) K ¹⁺ + 0.29 Na ¹⁺	3.406	X(4)
** X(6)	--	8	10	0.211(4) Na ¹⁺ + 0.789□	0.27 Na + 0.73□	0.397(6) Na ¹⁺ + 0.603□	3.935	0(11)
** X(7)	--	4	12	0.070(14) Na ¹⁺ + 0.930□	0.17 Na + 0.83□	0.075(14) Na ¹⁺ + 0.925□		
** P(1)	P(5)	8	4	0.789(4) P ⁰⁺ + 0.211□	0.73 P + 0.27□	0.603(6) P ⁰⁺ + 0.397□		
** O(3)	C(19)	8	8	0.789(4) O ¹⁻ + 0.211□	1.00 O	0.603(6) O ¹⁻ + 0.397□		
** O(4)	O(20)	8	8	0.789(4) O ¹⁻ + 0.211□	0.73 O + 0.27□	0.603(6) O ¹⁻ + 0.397□		
** P(1x)	--	8	4	0.211(4) P ⁰⁺ + 0.789□	0.27 P + 0.73□	0.397(6) P ⁰⁺ + 0.603□		
** O(3x)	--	8	8	0.211(4) O ¹⁻ + 0.789□	0.27 O + 0.73□	0.397(6) O ¹⁻ + 0.603□		
** O(4x)	--	8	8	0.211(4) O ¹⁻ + 0.789□	identical to O(3)	0.397(6) O ¹⁻ + 0.603□		

*† Headed as atomic label in this paper, labels of Krutik et al. (1979) (KPPB), equipoint rank number (ERN), coordination number (CN), site occupancy and scattering curves used, the next larger distance in the structure not listed in Table 6. If the last entry is a potential coordinating anion it is underlined. If CN is included parenthetically, this implies the distance stated in the last entry.

† Assuming full occupancy, site population is approximately NM = 0.59 Fe²⁺ + 0.41 Li¹⁺ and BR = 0.41 Fe²⁺ + 0.59 Li¹⁺. Assuming total site population equals the [1-X(6)] population this gives NM = 0.35 Fe²⁺ + 0.44 Li¹⁺ + 0.21□ and BR = 0.17 Fe²⁺ + 0.43 Li¹⁺ + 0.40□.

*,** Partly occupied sites.

** Sites whose populations are coupled to each other.

Table 9. Arrojadite (NM): electrostatic valence balance of cations and anions[†]

	Coordinating Cations									
	M(1)	M(2)	M(3)	M(4)	M(5)	M(6)	M(7)	A1	X(1)	X(2)
Bond strength:	3/8	2/5	2/6	2/6	2/6	2/6	2/5	3/6	1/8	1/7
<u>Anions</u>										
O(1)	-----	-----	<u>+0.057</u>	-0.053	-----	-----	-----	-----	-----	-----
O(2)	-----	-----	-----	-----	<u>-0.042</u>	+0.048	-----	-----	-----	-----
O(3)	-----	<u>-0.023</u>	-----	-----	-----	-----	-----	-----	-----	-----
O(4)	<u>-0.053</u>	-----	-----	-----	-----	-----	-----	-----	<u>-0.116</u>	-----
O(5)	-----	-----	-----	<u>+0.051</u>	-----	-----	-----	-0.022	-----	-----
O(6)	-----	-----	-----	-----	<u>-0.044</u>	<u>-0.055</u>	-----	-----	-----	-----
O(7)	-----	-----	-----	<u>+0.007</u>	-----	-----	-0.059	-----	<u>+0.336</u>	-----
O(8)	<u>+0.000</u>	-----	-----	-----	-----	-----	-----	-----	<u>-0.249</u>	-----
O(9)	-----	-----	<u>+0.058</u>	<u>+0.001</u>	-----	-----	-----	-----	<u>-0.006</u>	-----
O(10)	-----	-----	-----	-----	-----	-----	-----	+0.011	-----	<u>-0.171</u>
O(11)	<u>+0.032</u>	-----	-----	-----	-0.005	-----	-----	-----	-----	-----
O(12)	+0.020	-----	-----	-----	-----	<u>-0.039</u>	-----	-----	-----	-----
O(13)	-----	-----	-----	-----	<u>+0.140</u>	-----	-----	<u>+0.012</u>	-----	-0.154
O(14)	-----	-----	-0.070	-----	<u>+0.072</u>	-----	-----	-----	-----	-----
O(15)	-----	-----	-----	+0.073	-----	-----	-----	-----	<u>-0.179</u>	-----
O(16)	-----	-----	-----	-----	-----	-----	+0.016	-----	<u>+0.344</u>	-----
O(17)	-----	-----	-----	-----	-----	-----	-----	-----	<u>-0.242</u>	+0.222
O(18)	-----	-----	-----	-----	<u>-0.121</u>	-----	-----	-----	<u>+0.107</u>	+0.185
O(19)	-----	-----	-----	-----	-----	<u>-0.163</u>	-----	-----	-----	-----
O(20)	-----	<u>-0.026</u>	+0.058	-----	-----	-----	-----	-----	-----	-----
O(21)	-----	<u>+0.013</u>	-----	-----	-----	-----	+0.030	-----	-----	-0.070
O(22)	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
O(23)	-----	<u>+0.020</u>	-0.060	-----	-----	-----	-----	-----	-----	-----
O(24)	-----	<u>+0.017</u>	-----	-----	-----	<u>+0.170</u>	-----	-----	-----	-0.095
F	-----	-----	-0.044	-----	-----	<u>+0.041</u>	<u>+0.106</u>	-----	-----	-----

[†]A bond length deviation refers to the polyhedral average subtracted from the individual bond distance. The Δp_0 = deviation of electrostatic bond strength sum from neutrality ($p_0 = 2.00$ v.u.). Bond length deviations which conform to Δp_0 are underlined.

Table 11. Arrojadite-dickinsonite cations in cell based on 200 (O²⁻, F⁻, OH⁻) anions

	1	2	3	4	5	6	7	8	9	10	11	12
Al ³⁺	4.40	4.06	3.28	4.51	3.61	3.63	3.88	3.88	3.26	3.22	3.16	
Fe ³⁺	--	--	1.52	--	1.76	0.20	--	--	--	--	12.40	
Mg ²⁺	2.18	3.27	5.92	2.76	13.89	9.08	7.09	5.16	--	3.39	3.69	
Mn ²⁺	18.79	17.11	23.36	4.11	16.98	8.43	9.48	14.83	37.38	36.80	13.98	
Fe ²⁺	33.17	33.55	22.96	41.52	20.23	32.17	40.39	35.93	15.02	14.08	22.20	
Zn ²⁺	--	0.26	--	--	0.20	0.18	0.24	0.06	--	--	--	
Li ¹⁺	0.51	1.89	1.14	--	3.88	1.34	2.95	0.46	1.22	1.10	--	
Sum	59.05	60.14	57.98	52.90	60.55	55.03	64.03	60.32	56.88	58.59	55.49	60
Na ⁺	17.44	15.17	13.66	19.64	12.07	14.30	14.68	17.76	19.80	19.61	12.11	
K ⁺	3.12	1.02	1.14	1.87	1.02	1.63	2.58	2.46	3.18	3.01	2.47	
Ca ²⁺	3.70	1.26	3.46	7.75	3.79	3.27	5.52	1.95	3.10	2.94	8.16	
Sr ²⁺	--	0.26	--	--	0.28	0.10	0.04	0.53	--	--	--	
Ba ²⁺	--	2.42	2.98	--	0.81	1.21	0.01	0.11	--	--	--	
Pb ²⁺	--	0.29	--	--	1.63	0.32	0.13	--	--	--	--	
Sum	24.26	20.42	21.24	29.26	19.60	20.83	22.96	22.81	26.08	25.56	22.74	24
Total	83.31	80.56	79.22	82.16	80.15	75.86	86.99	83.13	82.96	84.15	78.23	
p ⁵⁺	47.59	47.31	47.23	48.0	47.23	48.0	47.95	48.0	47.98	47.12	38.87	48
F ⁻	3.55	4.29	2.11	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	
H ₂ O ⁺	4.26	3.86	6.86	N.D.	7.57	4.38	0.66	N.D.	7.54	8.28	22.13	8
H ₂ O ⁻	--	2.15	0.47	--	--	--	--	--	--	--	1.96	
O = F	1.78	2.15	1.05	--	--	--	--	--	--	--	--	

1. Nickel Plate Mine (see Moore and Ito, 1979, on this and subsequent analyses); 2. Sidi-bou Kricha;
 3. Buranga Mine; 4. Victory Mine; 5. Sapucaia pegmatite; 6. Smith Mine; 7. Nancy Mine; 8. Palermo
 No. 1 Mine; 9. Branchville; 10. Berry Quarry; 11. Serra Branca Mine; 12. Theoretical contents for
 [Al₄Fe₆][Na, K, Ca]₂₄[PO₄]₄₈(OH)₈.