AM-81-171/172/173

American Mineralogist, Volume 66, pages 1034–1049, 1981

The arrojadite–dickinsonite series, $KNa_4Ca(Fe,Mn)^{2+}_{14}Al(OH)_2(PO_4)_{12}$: crystal structure and crystal chemistry

PAUL B. MOORE AND TAKAHARU ARAKI

Department of the Geophysical Sciences
The University of Chicago
Chicago, Illinois 60637

STEFANO MERLINO AND MARCELLO MELLINI

Istituto di Mineralogia
Università di Pisa
56100 Pisa, Italy

AND PIER FRANCESCO ZANAZZI

Istituto di Mineralogia
Università di Perugia
06100 Perugia, Italy

Abstract

The complex crystal structure of the arrojadite–dickinsonite, $KNa_4Ca(Fe,Mn)^{2+}_{14}Al(OH,F)_2(PO_4)_{12}$, 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)Å, β = 105.60(2)°, 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 wyllieite, $Na_2Fe^{2+}_2Al(PO_4)_3$, 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 $\sum(M+X):\sum(P) = 5:3$ as for wyllieite. Average bond distances in dickinsonite are

$^{[4]}$M(1)–O 2.092,	$^{[5]}$M(2)–O 2.133,	$^{[6]}$M(3)–O 2.156,	$^{[6]}$M(4)–O 2.167,
$^{[6]}$M(5)–O 2.166,	$^{[6]}$M(6)–O 2.235,	$^{[5]}$M(7)–O 2.190,	$^{[6]}$Al–O 1.884,
$^{[8]}$X(1)–O 2.516,	$^{[7]}$X(2)–O 2.515,	$^{[8]}$X(3)–O 2.574,	$^{[10]}$X(4)–O 3.012,
$^{[8]}$X(5)–O 2.928,	$^{[10]}$X(6)–O 2.940,	$^{[12]}$X(7)–O 3.080 Å	

The sites M(1), X(1), X(4), X(6), and X(7) are disordered. In addition, one of the six nonequivalent (PO_4) tetrahedra is disordered, with evidence of splitting into a reciprocally coupled P(1x) 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 tumultous investigative history. *Arrojadite* was originally named by Guimarães (1942) for material from the Serra Branca pegmatite,

0003-004X/81/0910-1034$02.00

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

Atom	KPPB	ERN	CN	Occupancy NM	Occupancy NP	Occupancy BR	Next larger in crystal 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 O(12)
M(2)	X(5)	8	5	1.0 Fe^{2+}	1.0 Fe	1.0 Mn^{2+}	3.017 O(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 O(10)
M(5)	X(1)	8	6	1.00 Fe^{2+}	1.0 Fe	0.5 Mn^{2+} + 0.5 Fe^{2+}	3.206 O(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 O(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 O(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 O(5)
X(3)	A(2)	4	8	1.0 Na^{1+}	1.0 Na	1.0 Na^{1+}	3.506 O(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 O(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 O(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)	O(19)	8		0.789(4) O^{1-} + 0.211□	1.00 O	0.603(6) O^{1-} + 0.397□	
** O(4)	O(20)	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		0.211(4) O^{1-} + 0.789□	0.27 O + 0.73□	0.397(6) O^{1-} + 0.603□	
** O(4x)	--	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 Fe^{2+} + 0.41 Li^{1+} and BR = 0.41 Fe^{2+} + 0.59 Li^{1+}. Assuming total site population equals the [1-X(6)] population this gives NM = 0.35 Fe^{2+} + 0.44 Li^{1+} + 0.21□ and BR = 0.17 Fe^{2+} + 0.43 Li^{1+} + 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)	Al	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
Anions										
O(1)	------	------	+0.057	-0.053	------	------	------	------	------	------
O(2)	------	------	------	------	-0.042	+0.048	------	------	------	------
O(3)	------	-0.023	------	------	------	------	------	------	------	------
O(4)	-0.053	------	------	------	------	------	------	------	-0.116	------
O(5)	------	------	------	+0.051	------	------	------	-0.022	------	------
O(6)	------	------	------	------	-0.044	-0.055	------	------	------	------
O(7)	------	------	------	+0.007	------	------	-0.059	------	+0.336	------
O(8)	+0.000	------	------	------	------	------	------	------	-0.249 -0.006	------
O(9)	------	------	+0.058	+0.001	------	------	------	------	------	------
O(10)	------	------	------	------	------	------	------	+0.011	------	-0.171
O(11)	+0.032	------	------	------	-0.005	------	------	------	------	------
O(12)	+0.020	------	------	------	------	-0.039	------	------	------	------
O(13)	------	------	------	------	+0.140	------	------	+0.012	------	-0.154
O(14)	------	------	-0.070	------	+0.072	------	------	------	------	------
O(15)	------	------	------	+0.073	------	------	------	------	-0.179 +0.344	------
O(16)	------	------	------	------	------	------	+0.016	------	-0.242 +0.107	+0.222
O(17)	------	------	------	------	-0.121	------	------	------	------	+0.185
O(18)	------	------	------	------	------	-0.163	------	------	------	------
O(19)	------	-0.026	+0.058	------	------	------	------	------	------	------
O(20)	------	+0.013	------	------	------	------	+0.030	------	------	-0.070
O(21)	------	------	------	-0.078	------	------	------	------	------	+0.084
O(22)	------	------	------	------	------	------	-0.094	------	------	------
O(23)	------	+0.020	-0.060	------	------	------	------	------	------	------
O(24)	------	+0.017	------	------	------	+0.170	------	------	------	-0.095
F	------	------	-0.044	------	------	+0.041	+0.106	------	------	------

†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 9 (continued)

	Coordinating Cations									
	X(3)	X(4)	X(5)	P(1)	P(2)	P(3)	P(4)	P(5)	P(6)	Δp_o
Bond strength:	1/8	1/10	1/8	5/4	5/4	5/4	5/4	5/4	5/4	
Anions:										
O(1)	------	-0.090	------	+0.025	------	------	------	------	------	+0.02
O(2)	------	------	------	-0.014	------	------	------	------	------	-0.08
O(3)	------	-0.492	------	-0.032	------	------	------	------	------	-0.25
O(4)	------	------	------	+0.021	------	------	------	------	------	-0.25
O(5)	------	------	------	------	+0.017	------	------	------	------	+0.08
O(6)	------	------	------	------	-0.020	------	------	------	------	-0.08
O(7)	------	------	------	-------	+0.011	------	------	------	------	+0.11
O(8)	------	------	------	------	-0.010	------	------	------	------	-0.25
O(9)	+0.043	------	------	------	------	-0.008	------	------	------	+0.04
O(10)	------	------	------	-----	------	-0.009	------	------	------	-0.11
O(11)	+0.205	------	------	------	------	+0.009	------	------	------	+0.08
O(12)	------	------	------	------	------	+0.008	------	------	------	-0.04
O(13)	------	------	------	------	------	------	+0.019	------	------	+0.23
O(14)	-0.207	------	------	------	------	------	+0.006	------	------	+0.04
O(15)	-0.041	------	------	------	------	------	-0.013	------	------	-0.17
O(16)	------	------	------	------	------	------	-0.013	------	------	-0.08
O(17)	------	------	+0.016	------	------	------	------	-0.012	------	-0.15
O(18)	------	------	-0.169	------	------	------	------	-0.017	------	-0.08
O(19)	------	------	------	------	------	------	------	+0.009	------	-0.02
O(20)	------	------	------	------	------	------	------	+0.020	------	+0.19
O(21)	------	+0.378	+0.184	------	------	------	------	------	-0.002	-0.05
O(22)	------	+0.300	-0.031	------	------	------	------	------	-0.007	-0.12
O(23)	------	-0.096	------	------	------	------	------	------	-0.004	+0.08
O(24)	------	------	------	------	------	------	------	------	+0.014	+0.13
F	------	------	------	------	------	------	------	------	------	+0.07

Table 11. Arrojadite-dickinsonite cations in cell based on 200 (O^{2-}, 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+}	--	--	1.32	--	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_2O^+	4.26	3.86	6.86	N.D.	7.57	4.38	0.66	N.D.	7.54	8.28	22.13	8
H_2O^-	--	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 $[Al_4Fe_{56}][(Na,K,Ca)]_{24}[PO_4]_{48}(OH)_8$.