

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

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## Abstract

The complex crystal structure of the arrojadite-dickinsonite,  $\text{KNa}_4\text{Ca}(\text{Fe,Mn})_{14}^{2+}\text{Al}(\text{OH},\text{F})_2(\text{PO}_4)_{12}$ , 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,  $\text{Na}_2\text{Fe}_2^{2+}\text{Al}(\text{PO}_4)_3$ , 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

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

The sites M(1), X(1), X(4), X(6), and X(7) are disordered. In addition, one of the six non-equivalent  $(\text{PO}_4)$  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 3. Arrojadite-dickinsonite: anisotropic thermal vibration parameters ( $\times 10^3$ )<sup>†</sup>

	U <sub>11</sub>		U <sub>22</sub>		U <sub>33</sub>		U <sub>12</sub>		U <sub>13</sub>		U <sub>23</sub>	
	NM	BR	NM	BR	NM	BR	NM	BR	NM	BR	NM	BR
M(1)	312(7)	214(9)	197(7)	184(8)	193(6)	164(8)	-129(6)	-34(6)	154(5)	52(6)	-87(5)	-42(6)
M(2)	132(3)	195(4)	132(3)	200(4)	190(3)	251(4)	-2(2)	11(3)	46(2)	10(3)	10(2)	-13(3)
M(3)	95(4)	176(3)	93(4)	183(4)	147(4)	191(3)	-7(3)	-12(3)	33(3)	32(3)	9(3)	5(3)
M(4)	163(3)	210(4)	125(3)	185(4)	175(3)	201(4)	-20(2)	-15(3)	82(2)	45(3)	-24(2)	-30(3)
M(5)	120(3)	179(3)	131(3)	200(4)	152(3)	152(3)	-1(2)	6(3)	54(2)	31(3)	3(2)	-12(3)
M(6)	110(3)	167(4)	193(3)	201(4)	183(3)	193(4)	4(2)	10(3)	52(2)	39(3)	-13(2)	-15(3)
M(7)	114(3)	195(4)	288(1)	249(5)	177(3)	200(4)	-18(3)	-33(3)	62(2)	22(3)	66(3)	32(3)
A1	79(7)	161(9)	65(7)	174(9)	89(7)	168(9)	-1(5)	-1(6)	49(5)	50(6)	1(5)	36(6)
X(1)	391(14)	252(10)	275(12)	226(10)	303(12)	213(10)	214(9)	69(7)	284(10)	127(8)	175(8)	52(7)
X(2)	202(11)	279(14)	164(11)	234(13)	1329(36)	870(28)	-39(9)	-19(10)	-270(17)	-127(15)	169(16)	72(14)
X(3)	231(14)	337(20)	165(14)	240(18)	409(19)	421(22)	-3(11)	11(14)	-89(14)	-45(16)	49(12)	64(15)
X(4)	297(52)	2945(217)	1564(100)	1972(161)	231(30)	1220(101)	0	0	24(24)	1736(136)	0	0
X(5)	907(19)	1577(51)	361(11)	586(25)	282(9)	581(24)	0	0	339(10)	719(29)	0	0
P(1)	182(7)	187(13)	94(6)	156(9)	136(6)	181(10)	31(5)	-2(7)	106(5)	75(9)	1(4)	-23(7)
O(1)	239(15)	269(18)	117(14)	225(18)	171(14)	206(17)	-21(12)	-10(15)	123(12)	97(14)	-1(11)	6(14)
O(2)	245(15)	283(19)	115(13)	165(16)	193(15)	274(19)	26(12)	21(14)	140(13)	120(15)	27(11)	8(14)
O(3)	860(69)	202(30)	249(45)	138(26)	921(76)	261(30)	246(42)	69(22)	801(60)	168(26)	195(44)	15(22)
O(4)	420(29)	247(32)	189(23)	260(33)	230(23)	244(32)	-47(21)	-1(26)	-23(21)	-9(25)	-45(18)	-55(26)
P(2)	121(4)	194(6)	98(4)	176(6)	112(4)	160(5)	-7(3)	-12(4)	68(3)	63(4)	-2(3)	15(4)
O(5)	152(13)	241(17)	95(13)	193(17)	136(13)	169(16)	2(10)	8(14)	95(11)	72(13)	2(10)	-34(13)
O(6)	228(15)	228(17)	116(13)	224(18)	191(15)	191(16)	25(12)	41(14)	147(12)	86(14)	3(11)	7(14)
O(7)	218(15)	258(18)	135(14)	236(18)	175(14)	173(16)	-70(12)	-72(15)	130(12)	75(14)	-23(11)	-43(14)
O(8)	209(16)	240(19)	295(19)	351(22)	146(14)	181(17)	-56(14)	-49(17)	37(12)	13(14)	-1(13)	-19(16)
P(3)	89(4)	165(5)	89(4)	172(6)	96(4)	157(5)	13(3)	-1(4)	47(3)	33(4)	13(3)	15(4)
O(9)	155(13)	229(17)	141(14)	224(18)	176(14)	211(17)	35(11)	8(14)	92(11)	97(14)	9(11)	14(14)
O(10)	127(12)	227(17)	75(12)	202(18)	126(12)	218(17)	-0(10)	-22(14)	33(10)	39(14)	15(10)	22(14)
O(11)	83(12)	164(16)	155(14)	238(18)	204(15)	247(18)	18(10)	28(14)	37(11)	13(13)	-57(12)	-61(15)
O(12)	199(15)	260(19)	145(14)	272(20)	115(13)	163(16)	52(12)	52(15)	26(11)	16(14)	17(11)	15(14)
P(4)	90(4)	175(5)	80(4)	156(5)	126(4)	155(5)	-12(3)	-6(4)	49(3)	31(4)	-9(3)	10(4)
O(13)	109(12)	243(17)	90(12)	171(16)	133(12)	166(15)	-31(10)	-6(13)	59(10)	62(13)	-22(10)	-11(13)
O(14)	115(12)	235(17)	99(13)	176(17)	182(14)	198(16)	-24(10)	-13(14)	66(11)	58(14)	-0(11)	6(13)
O(15)	105(12)	183(17)	142(14)	200(18)	257(16)	371(22)	1(11)	-6(14)	69(12)	41(15)	26(12)	41(16)
O(16)	196(15)	335(21)	229(17)	248(20)	120(13)	171(17)	-38(13)	-55(16)	7(12)	-15(15)	10(12)	35(14)
P(5)	90(4)	168(5)	88(4)	153(6)	174(5)	186(6)	3(3)	-0(4)	34(4)	20(4)	11(4)	16(4)
O(17)	174(15)	248(19)	230(17)	300(21)	202(16)	202(18)	-1(13)	19(16)	27(13)	1(14)	1(13)	-25(15)
O(18)	131(14)	188(17)	243(18)	294(21)	322(19)	288(20)	28(13)	17(15)	76(13)	58(15)	25(14)	-21(16)
O(19)	202(16)	247(20)	98(15)	172(18)	471(24)	477(27)	35(12)	17(15)	-44(17)	-37(18)	-12(18)	-12(18)
O(20)	146(14)	255(18)	225(17)	257(20)	211(16)	204(17)	11(12)	8(15)	66(12)	64(14)	24(13)	27(14)
P(6)	113(4)	161(5)	90(5)	167(6)	260(6)	201(6)	2(4)	-19(4)	-12(4)	5(4)	-13(4)	13(4)
O(21)	143(14)	251(19)	177(16)	256(20)	278(18)	249(19)	2(12)	-28(16)	-22(13)	-28(15)	-4(14)	72(15)
O(22)	135(16)	197(19)	225(20)	337(25)	856(39)	600(33)	-52(14)	-92(18)	-31(21)	-40(20)	126(23)	234(23)
O(23)	97(13)	236(18)	79(13)	141(16)	396(20)	311(20)	0(10)	4(14)	14(13)	15(15)	-4(13)	33(14)
O(24)	364(21)	326(21)	228(19)	227(19)	235(18)	215(18)	72(16)	32(16)	-14(16)	70(15)	-71(15)	-25(15)
F	363(18)	369(21)	295(18)	324(21)	193(14)	360(20)	1(13)	43(15)	90(13)	128(16)	17(12)	27(15)

<sup>†</sup>Coefficients in the expression  $\exp[-U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl]$ . Estimated standard errors in parentheses refer to the last digit. The disordered cations X(6), X(7), P(1x), O(3x) and O(4x) were examined isotropically.