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## Crystal structure of arrojadite

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The crystal structure of the Na, Fe, Mn phosphate arrojadite is determined (single-crystal diffractometer,  $\lambda$  Mo, 4102 reflections, method of least squares in isotropic approximation to  $R = 0.135$ ). The parameters of the monoclinic lattice are:  $a = 16.476$  (4);  $b = 24.581$  (5);  $c = 9.996$  (3) Å;  $\gamma = 105.79$  (2)°, sp. gr.  $B2/b$ . The structure is based on a three-dimensional framework of (Fe,Mn) polyhedra (octahedra, semioctahedra, and tetrahedra). Three of the eight independent positions of Fe and Mn can enclose the lighter Al, Mg, and Li. The large cations Na, K, Ca, Ba, and Sr lie in the gaps in the structure. The P orthotetrahedra join up the structural elements (layers and tubes) of the three-dimensional framework of (Fe,Mn) polyhedra. The expanded structural formula of arrojadite is  $\text{Na}_{0.5}(\text{Na}, \text{K}, \text{Ba}, \text{Sr})_{0.5}(\text{Fe}, \text{Mn})_5\text{Al}_{0.5}(\text{Li}, \text{Mg}, \text{Ca}, \text{Al}, \text{Fe}, \text{Mn})_2(\text{PO}_4)_4[\text{PO}_3(\text{O}, \text{F}, \text{OH})]_2(\text{OH})$ , with  $Z = 8$ .

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The crystal-structural study of natural phosphates, which are the third most widely distributed minerals in the earth's crust after silicates and oxides, is of interest both to descriptive and to genetic mineralogy. As emphasized in Ref. 1, the variety of endogenous phosphates<sup>1)</sup> must be regarded as due to the relatively narrow regions of thermodynamic stability of each mineral of this class. If so, then phosphate minerals may serve as natural indicators of the formation conditions of the rocks containing them. A study of these questions would not be possible without a detailed structural investigation of phosphates and an elucidation of the genetic relations between their main structural components.

The structure of arrojadite, which belongs to the very widespread but crystallochemically little studied group of Na(Fe, Mn) phosphates, was elucidated in the course of an investigation of natural and synthetic minerals with large (Na, Ca, Sr, Ba) and medium (Mn, Fe, Zn) cations, made at the Department of Crystallography and Crystal Chemistry of Moscow University. A mineralogical investigation<sup>4</sup> undertaken immediately after the discovery of arrojadite<sup>3</sup> established the parameters of its monoclinic lattice:  $a = 16.60$ ;  $b = 10.02$ ;  $c = 23.99$  Å;  $\beta = 93^\circ 37'$ , space group  $C2/m$ ; arrojadite and the mineral dickinsonite, of similar composition, were considered separately from one another. Later Fisher<sup>5,6</sup> compared their powder patterns

TABLE I. Coordinates of Basis Atoms and Individual Temperature Corrections for Arrojadite Structure

Atom	$x/a$	$y/b$	$z/c$	$B$	Atom	$x/a$	$y/b$	$z/c$	$B$
X <sub>1</sub>	0.4664	0.6001	0.2550	0.84	O <sub>5</sub>	0.2908	0.0285	0.4631	1.64
X <sub>2</sub>	0.4783	0.5969	0.7497	1.42	O <sub>6</sub>	0.1201	0.3904	0.0975	1.24
X <sub>3</sub>	0.2958	0.6478	0.2988	1.12	O <sub>7</sub>	0.3709	0.6138	0.6580	1.06
X <sub>4</sub>	0.2816	0.6570	0.7057	1.58	O <sub>8</sub>	0.4491	0.5549	0.5561	0.47
X <sub>5</sub>	0.2882	0.7327	-0.0113	1.02	O <sub>9</sub>	0.4414	0.3348	0.3465	1.10
X <sub>6</sub>	0.3936	0.3601	0.0155	0.86	O <sub>10</sub>	0.2824	0.3170	0.3583	1.49
X <sub>7</sub>	0.2218	0.4761	0.3920	1.52	O <sub>11</sub>	0.3491	0.2354	0.3548	1.83
X <sub>8</sub>	0	0	0	0.85	O <sub>12</sub>	0.3518	0.2941	0.1418	0.85
A <sub>1</sub>	0	0.25	-0.0018	0.71	O <sub>13</sub>	0.4534	0.3293	0.6754	1.18
A <sub>2</sub>	0.50	0.50	0	1.81	O <sub>14</sub>	0.2938	0.3062	0.6665	1.29
A <sub>3</sub>	0.1331	0.1207	0.0155	0.89	O <sub>15</sub>	0.3683	0.2291	0.6744	1.14
P <sub>1</sub>	0.3734	0.4606	0.2512	0.37	O <sub>16</sub>	0.1298	0.2105	0.3813	1.86
P <sub>2</sub>	0.3694	0.5765	0.5340	0.51	O <sub>17</sub>	0.3682	0.6380	0.1392	1.10
P <sub>3</sub>	0.3569	0.2946	0.3004	0.64	O <sub>18</sub>	0.4748	0.1320	0.0630	0.89
P <sub>4</sub>	0.3734	0.2879	0.7260	0.47	O <sub>19</sub>	0.3545	0.1765	0.0799	2.04
P <sub>5</sub>	0.3864	0.6928	-0.0102	2.12	O <sub>20</sub>	0.3179	0.0741	0.0405	4.05
P <sub>6</sub>	0.3981	0.4523	0.7684	0.55	O <sub>21</sub>	0.0457	0.0485	0.1463	0.49
O <sub>1</sub>	0.3913	0.5197	0.1878	0.94	O <sub>22</sub>	0.0640	0.0800	0.3704	0.79
O <sub>2</sub>	0.2766	0.4363	0.2568	1.46	O <sub>23</sub>	0.1952	0.0766	0.2340	1.02
O <sub>3</sub>	0.4146	0.4236	0.1662	0.70	O <sub>24</sub>	0.4053	0.0133	0.1853	1.02
O <sub>4</sub>	0.4043	0.4631	0.3958	0.68	O <sub>25</sub>	0.2311	0.1392	0.4979	1.41

TABLE II. Interatomic Distances (in angstroms) in the Arrojadite Structure

X-polyhedra			
X <sub>1</sub> -O <sub>13</sub>	2.000	X <sub>2</sub> -O <sub>9</sub>	2.073
-O <sub>6</sub>	2.102	-O <sub>7</sub>	2.127
-O <sub>17</sub>	2.123	-O <sub>3</sub>	2.143
-O <sub>1</sub>	2.133	-O <sub>24</sub>	2.180
-O <sub>24</sub>	2.273	-O <sub>8</sub>	2.184
-O <sub>22</sub>	2.203	-O <sub>18</sub>	2.071
Mean	2.139	Mean	2.130
X <sub>4</sub> -O <sub>14</sub>	2.023	X <sub>5</sub> -O <sub>12</sub>	2.079
-O <sub>7</sub>	2.088	-O <sub>19</sub>	2.092
-O <sub>23</sub>	2.141	-O <sub>16</sub>	2.105
-O <sub>14</sub>	2.144	-O <sub>10</sub>	2.105
-O <sub>25</sub>	2.218	-O <sub>14</sub>	2.111
-O <sub>19</sub>	2.434	Mean	2.099
Mean	2.175	Mean	2.107
X <sub>7</sub> -O <sub>23</sub>	1.977	X <sub>8</sub> -O <sub>8</sub>	1.860
-O <sub>2</sub>	2.014	-O <sub>8'</sub>	1.860
-O <sub>1</sub>	2.055	-O <sub>4</sub>	1.902
-O <sub>5</sub>	2.065	-O <sub>4'</sub>	1.902
Mean	2.028	-O <sub>21</sub>	1.906
		-O <sub>21'</sub>	1.908
		Mean	1.890
P-tetrahedra			
P <sub>1</sub> -O <sub>1</sub>	1.527	P <sub>2</sub> -O <sub>5</sub>	1.499
-O <sub>2</sub>	1.530	-O <sub>6</sub>	1.532
-O <sub>3</sub>	1.539	-O <sub>7</sub>	1.538
-O <sub>4</sub>	1.547	-O <sub>8</sub>	1.555
Mean	1.536	Mean	1.531
O <sub>2</sub> -O <sub>2</sub>	2.516	O <sub>5</sub> -O <sub>6</sub>	2.518
-O <sub>3</sub>	2.504	-O <sub>7</sub>	2.468
-O <sub>4</sub>	2.544	-O <sub>8</sub>	2.517
O <sub>2</sub> -O <sub>3</sub>	2.543	O <sub>6</sub> -O <sub>7</sub>	2.562
-O <sub>4</sub>	2.456	-O <sub>8</sub>	2.509
O <sub>3</sub> -O <sub>4</sub>	2.479	O <sub>7</sub> -O <sub>8</sub>	2.411
P <sub>4</sub> -O <sub>13</sub>	1.552	P <sub>5</sub> -O <sub>17</sub>	1.507
-O <sub>14</sub>	1.568	-O <sub>18</sub>	1.515
-O <sub>15</sub>	1.524	-O <sub>19</sub>	1.490
-O <sub>16</sub>	1.552	-O <sub>20</sub>	1.578
Mean	1.550	Mean	1.522
O <sub>13</sub> -O <sub>14</sub>	2.535	O <sub>17</sub> -O <sub>18</sub>	2.479
-O <sub>15</sub>	2.481	-O <sub>19</sub>	2.519
-O <sub>16</sub>	2.518	-O <sub>20</sub>	2.469
O <sub>14</sub> -O <sub>15</sub>	2.524	O <sub>18</sub> -O <sub>19</sub>	2.493
-O <sub>16</sub>	2.579	-O <sub>20</sub>	2.604
O <sub>15</sub> -O <sub>16</sub>	2.542	O <sub>19</sub> -O <sub>20</sub>	2.480
A <sub>1</sub> -O <sub>8</sub>	2.734	A <sub>2</sub> -O <sub>13</sub>	2.350
-O <sub>8'</sub>	2.734	-O <sub>13'</sub>	2.350
-O <sub>1</sub>	2.824	-O <sub>20</sub>	2.500
-O <sub>1'</sub>	2.824	-O <sub>20'</sub>	2.500
-O <sub>6</sub>	2.889	-O <sub>12</sub>	2.613
-O <sub>6'</sub>	2.889	-O <sub>12'</sub>	2.613
-O <sub>2</sub>	2.934	-O <sub>10</sub>	2.728
-O <sub>2'</sub>	2.934	-O <sub>10'</sub>	2.728
Mean	2.845	Mean	2.548
X <sub>3</sub> -O <sub>15</sub>	2.046	X <sub>4</sub> -O <sub>12</sub>	2.047
-O <sub>6</sub>	2.139	-O <sub>23</sub>	2.054
-O <sub>2</sub>	2.162	-O <sub>25</sub>	2.065
-O <sub>25</sub>	2.257	-O <sub>3</sub>	2.129
-O <sub>17</sub>	2.261	-O <sub>18</sub>	2.143
-O <sub>10</sub>	2.349	-O <sub>13</sub>	2.201
Mean	2.202	Mean	2.107
P <sub>3</sub> -O <sub>9</sub>	1.545	P <sub>6</sub> -O <sub>21</sub>	1.532
-O <sub>10</sub>	1.577	-O <sub>22</sub>	1.529
-O <sub>11</sub>	1.542	-O <sub>23</sub>	1.506
-O <sub>12</sub>	1.546	-O <sub>24</sub>	1.553
Mean	1.551	Mean	1.530
O <sub>9</sub> -O <sub>10</sub>	2.533	O <sub>21</sub> -O <sub>22</sub>	2.361
-O <sub>11</sub>	2.521	-O <sub>23</sub>	2.603
-O <sub>12</sub>	2.541	-O <sub>24</sub>	2.543
O <sub>10</sub> -O <sub>11</sub>	2.523	O <sub>22</sub> -O <sub>23</sub>	2.476
-O <sub>12</sub>	2.546	-O <sub>24</sub>	2.539
O <sub>11</sub> -O <sub>12</sub>	2.546	O <sub>23</sub> -O <sub>24</sub>	2.450
A <sub>3</sub> -O <sub>2</sub>	2.457		
-O <sub>3</sub>	2.425		
-O <sub>6</sub>	2.644		
-O <sub>7</sub>	2.454		
-O <sub>13</sub>	2.349		
-O <sub>17</sub>	2.323		
-O <sub>19</sub>	2.773		
Mean	2.489		

TABLE III. Calculation of Valence Balance in Arrojadite Structure\*

Atom	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>	X <sub>8</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>5</sub>	P <sub>6</sub>	Σ	Δ
O <sub>1</sub>	0.330						0.466			0.104		1.229						2.129	0.129
O <sub>2</sub>			0.355				0.515					1.191						2.061	0.061
O <sub>3</sub>		0.321				0.313				0.116		1.299						2.049	0.049
O <sub>4</sub>							0.454	0.484			0.244	1.281						2.009	0.009
O <sub>5</sub>													1.442					1.896	0.104
O <sub>6</sub>	0.355		0.374										1.238					1.967	0.033
O <sub>7</sub>		0.333		0.390									1.205					1.928	0.012
O <sub>8</sub>		0.292						0.541					1.115					1.948	0.052
O <sub>9</sub>		0.379							0.116		0.219			1.290				2.004	0.004
O <sub>10</sub>			0.234		0.394						0.150			1.118				1.971	0.029
O <sub>11</sub>				0.450					0.127					1.308				1.891	0.109
O <sub>12</sub>					0.419	0.381								1.284				2.084	0.084
O <sub>13</sub>	0.456								0.120		0.181				1.232			1.990	0.010
O <sub>14</sub>				0.341	0.388						0.219				1.147			2.095	0.095
O <sub>15</sub>			0.467						0.138						1.400			2.005	0.005
O <sub>16</sub>					0.394	0.303									1.221			1.918	0.082
O <sub>17</sub>	0.338		0.284													1.325		1.947	0.053
O <sub>18</sub>		0.381				0.265										1.277		1.923	0.077
O <sub>19</sub>				0.181	0.406											1.435		2.022	0.022
O <sub>20</sub>							0.565									0.964		1.529	0.029
O <sub>21</sub>	0.240							0.476			0.250						1.235	2.201	0.201
O <sub>22</sub>	0.281					0.374				0.151							1.252	2.058	0.058
O <sub>23</sub>				0.344							0.162						1.392	1.898	0.102
O <sub>24</sub>		0.295								0.129							1.122	1.546	0.046
O <sub>25</sub>			0.266	0.288		0.365												0.939	0.061

\*The data in Table III enable us to assume that the O<sub>20</sub> and O<sub>24</sub> positions are filled by O<sup>2-</sup>, F<sup>-</sup>, and (OH)<sup>-</sup> anions, but the O<sub>25</sub> positions by mono-valent F<sup>-</sup> and (OH)<sup>-</sup> only.

and noticed that these minerals are very similar; he regarded them as the end members ("minally") of the isomorphous series from Mn-containing dickinsonite to Fe-arrojadite. The refined unit-cell parameters of arrojadite<sup>7</sup> are  $a = 24.78$ ;  $b = 10.05$ ;  $c = 16.15 \text{ \AA}$ ;  $\beta = 105^\circ 41'$ , space group C2/c; they confirm its similarity to dickinsonite.<sup>2)</sup> A detailed study of the chemical composition of arrojadite from a pegmatite vein at Sidi-Bu-Krish (Morocco)<sup>8</sup> revealed that this mineral can display cationic isomorphism over very wide limits; on this basis a new general formula was suggested:  $A_4X_{10}(PO_4)_8(F, OH)$ , where  $X = Fe^{2+}$ , Mn, Al, Ca, Mg, Li, Zn,  $A = Na, K, Ba, Sr, Pb(Ca), (Li)$ . The unit cell contains six formula units of this composition.

On the basis of this information we undertook a structural investigation of an arrojadite specimen from the "Nickel Plate" formation (USA), obtained from the collection of the Museum of the Institute of Geological Science of the Academy of Sciences of the Ukrainian SSR.

The x-ray data consisted of 4102 nonzero reflections from 22 layer lines ( $0kl - 21kl$ ), registered on a Syntex PI automatic diffractometer by the ( $2\theta; \theta$ ) method with variable scanning rate of 6-24° per minute (Mo radiation, graphite monochromator). The parameters of the monoclinic unit cell of arrojadite, refined on the same diffractometer, in a setting suitable for machine calculations, agreed with the data in Ref. 7:  $a = 16.476(4)$ ,  $b = 24.581(5)$ ,  $c = 9.996(3) \text{ \AA}$ ;  $\gamma = 105.79(2)^\circ$ . The systematic extinctions in the three-dimensional set of reflections with  $h + l = 2n + 1$  and  $k = 2n + 1$  ( $h = 2n + 1$ ) for the  $hk0$  reflections confirmed the Fedorov group to be B2/b (C2/c in the previous setting of the crystal axes<sup>7</sup>). By means of a Patterson synthesis we located the heavier X and A atoms in the general formula of arrojadite. The motif of these atoms is preserved with two types of arrangement in the unit cell differing by 0.25 times the b translation. The lower R index (0.32) and the better temperature corrections of the located atoms made it better to use a version with the  $X_8$  cations at the origin. A cycle of successive approximations (with the usual and zero Fourier syntheses) located the light atoms. The final coordinates of the basis atoms, listed in Table I, were obtained by refining the structure in the isotropic approximation to  $R = 0.135$ . It is hoped that refinement in the anisotropic approximation will be completed shortly. The interatomic distances in the cation polyhedra (Table II) were used to calculate the local valence balance on the anions (Table III), following Ref. 9, and pointed to the probable positions of the univalent  $F^-$  and  $(OH)^-$  ions. The balance quality criterion was about 0.033.

TABLE IV. Motifs from Cation Coordination (Fe, Mn) Polyhedra in Structures of Phosphate Minerals

Isolated	One-dimensional (columns and bands)	Two-dimensional (sheets)	Three-dimensional (frameworks)
Vivianite Strengite Leucophosphate	Strunzite Lapeite Ludlamite Barbosaltite Scorzalite Jansite Alusaudite Wiluite Stewartite	Eosphorite Rockbridgeite Beraunite Dufrenite Kryzhanovskite Phosphoferrite	Triphylite Sarcopside Nauophilite Whitemoreite Arrojadite

In a number of surveys of the crystal chemistry of phosphates, it is emphasized that the structures of all presently known natural compounds contain only isolated  $[PO_4]$  tetrahedra.<sup>3)</sup> Therefore, in contrast with the silicates, the classification of the phosphate minerals is based on the type of linkage of the cation polyhedra,<sup>11-13</sup> which play a leading part in the crystal structure.

In a description of the crystal structures of the main Fe and Mn phosphate minerals, Kabalov<sup>14</sup> showed that the Fe polyhedra (usually octahedra) can exist either in isolation or grouped into columns, bands, sheets, and three-dimensional frameworks (Table IV). Moore<sup>15</sup> has made an important contribution to the structural mineralogy of phosphates, which is not only of independent value, but is broadening our ideas on the widespread group of tetrahedral structures of transition metal compounds.

In arrojadite the X-polyhedra have different shapes (the  $X_{1-4,6,8}$ -octahedra,  $X_5$  semioctahedra, and  $X_7$ -tetrahedra), and this must be regarded as a consequence of the above-mentioned cation isomorphism. The X-polyhedra, which are interlinked, form an openwork three-dimensional framework (Fig. 1) in which the predominant structural elements are tubes extending along the dyad axes  $[001]$ , made up of three-tiered rings of  $X_{1-7}$  polyhedra. These hollow rods, which are linked via  $X_8$ -octahedra (each octahedron has common vertices with four rings belonging to two neighboring tubes), form wavy porous sheets parallel to (100) and joined along  $[100]$  via a common vertex  $O_{25} = (OH)^-$ . In the outer layers of the rings (with the central cations at the levels  $z \approx 0.25$  and  $z \approx -0.25$ ), gathered into the tubes, are links consisting of three and two X-polyhedra. In the links of three polyhedra the  $X_1$  and  $X_3$  octahedra are linked via a common edge, while the  $X_7$ -tetrahedron, which has one common vertex with each of the polyhedra, closes them into a botryoidal group. In another outer layer there are  $X_2$  and  $X_4$ -octahedra linked via vertices. The two outer

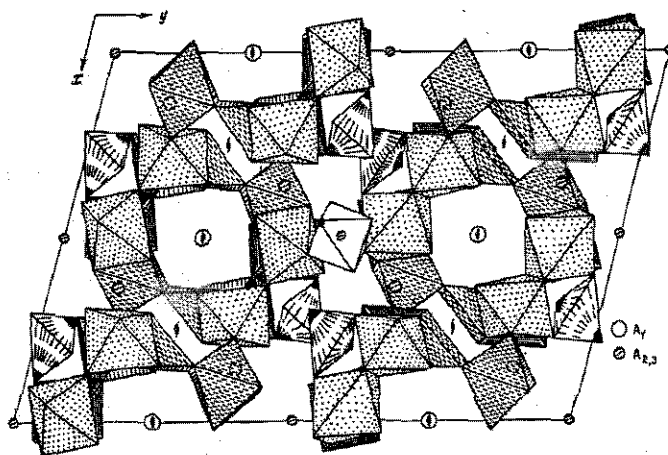


FIG. 1. Framework structure of X-polyhedra in xy projection in structure of arrojadite. Dotted shading marks octahedra of upper layer of three-tier rings gathered into tubes. Dashed-line shading marks  $X_5$ -semioctahedra and  $X_6$ -octahedra of central layer. Linked in pairs via edges; solid-line shading marks octahedra of bottom layers. Unshaded Al-octahedron ( $X_8$ -position) at center of projection links tubes along y axis. Outer layers of three-tier rings are supplemented by  $X_7$ -tetrahedra, marked by radial shading. On dyad axes are  $A_1$  atoms (Na, K, Ba, and Sr cations), shaded and dashed (hidden) circles are  $A_2$  (Na) and  $A_3$  (Na + Ca) cations.

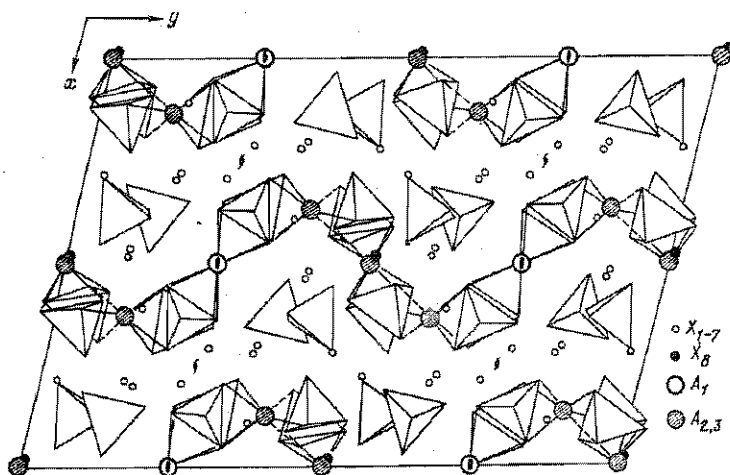


FIG. 2. P-orthotetrahedra in structure of arrojadite (xy projection). Black dots are Al cations ( $X_8$  positions), arbitrarily displaced from their positions at the inversion centers. At 0.5 of the c-translation from the Al cations there are Na cations ( $A_2$  positions). Bonds of A cations with O vertices of P tetrahedra are shown.

layers are fastened together by binuclear complexes of  $X_5$ -semioctahedra and  $X_6$ -octahedra, paired via an edge, with central cations lying near the square bases at the level  $z \approx 0$ . The rings translationally repeating along the z axis touch one another at a single point, the  $O_{25}$  vertex, which belongs simultaneously to the  $X_3$  and  $X_4$  octahedra, and they are thus condensed into tubes.

Refinement of the multiplicities of the cation positions X and A and analysis of the interatomic distances in their polyhedra supports our hypothesis concerning the arrangement of cations in the structure of arrojadite. The positions  $X_{1-5}$  apparently all correspond to Fe and Mn atoms. Considering that in all previously solved phosphates the Fe atoms lie in octahedra, it is natural to suppose that the positions  $X_{1-4}$  are occupied mainly by Fe, and the positions  $X_5$ , with fivefold coordination, by Mn atoms. In the remaining three positions X there are probably the lighter atoms Al, Mg, Li, and Ca, of which the total number in the cell, according to Huvelin et al.,<sup>8</sup> is about 10. The short distances in the  $X_8$  octahedra (av. 1.890 Å) show that Al atoms predominate in these. In the  $X_6$  octahedra and  $X_7$  tetrahedra there may be a statistical alternation of light atoms with Fe, Mn, and Zn atoms (in approximately the ratio 3 : 5). On these assumptions we get good agreement with the chemical analysis data: the total number of Fe and Mn atoms in the unit cell is about 50, and the total number of all atoms is  $X \approx 60$ .

Binuclear complexes of polyhedra paired via edges (like the  $X_{5-6}$  polyhedra in arrojadite) are characteristic of  $Mn^{2+}$  cations. Paired semioctahedra have already been found in  $K_2Mn_2Zn_4Si_4O_{15}$  (Ref. 16), and trigonal bipyramids with central  $Mn^{2+}$  ions, linked via edges, are present in the structure of  $Na_2Mn_2Si_2O_7$  (Ref. 17). One may note that in the Mn polyhedra paired via edges the distance between the central cations is shortened: in  $Na_2Mn_2Si_2O_7$  the Mn-Mn distance is about 3.5 Å, while in  $K_2Mn_2Zn_4Si_4O_{15}$  the Mn-Mn distance is about 3.0 Å, and in arrojadite  $X_5-X_6 \approx 3.2$  Å.

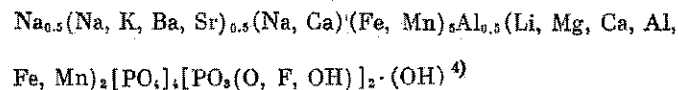
The large A cations occupy three positions in the structure. In one of these ( $A_1$ ) the (Na + K) and (Ba + Sr + Pb) atoms are statistically distributed in the ratio 1 : 1.

These cations link rings of  $X_{1-7}$  polyhedra along the z axis and are arranged within the hollow channels on the dyad axes. The coordination polyhedron of the  $A_1$  cations is formed by eight O atoms at the vertices of a slightly deformed cube (Fig. 2). The  $A_2$  cations, which are mainly Na atoms, occupy positions at the inversion centers, alternating along the z axes with the  $X_8$  octahedra. Their polyhedra are also deformed cubes, joining sets of four rings of X polyhedra within a sheet. In the gaps in the three-dimensional framework of X polyhedra there are  $A_3$  (Na + Ca) cations which fix the tube walls along [100]. The polyhedra of these atoms are formed by seven O atoms at the vertices of a single-capped pseudotrigonal prism.

In arrojadite the subordinate architectural role of the P-tetrahedra is clearly manifested. They are all isolated and tetradentate (each O vertex is common to at least one X polyhedron). The main function of the five P tetrahedra ( $P_{1-4,6}$ ) is to fix the bonds in the direction of the a axis between adjacent sheets (cores) of X and  $A_{1-2}$  polyhedra, distinguishable in the three-dimensional framework. We can assume that the P tetrahedra form torn "chain mail" similar to the "crumbled" Si chain mail in a number of silicate structures. A less important role belongs to the  $P_5$  tetrahedron, which takes part in the fixation of the upper and lower layers within the rings of  $X_{1-7}$  polyhedra.

The distances in the P tetrahedra are close to the usual values. The high value of  $B_j$  for the  $P_5$  atom may be evidence of some deficit of P atoms at these sites. The valence balance of the anions enables us to consider two positions of oxygen atoms ( $O_{20}$  and  $O_{24}$ ) in  $P_5$  and  $P_6$  tetrahedra as probable for the statistical arrangement of  $O^{2-}$ ,  $F^-$ , and  $(OH)^-$  anions, especially as the P-O distances are the greatest in the corresponding tetrahedra, and, as observed in many structures,<sup>18</sup> the P-(OH) or P-F distances are usually greater than P-O. One of these positions ( $O_{20}$ ) corresponds to a vertex which links the  $P_5$  and  $X_7$  tetrahedra and is characterized by a certain instability (comparatively high value of the thermal correction for  $O_{20}$ ).

In comparison with the published chemical analysis results the contents of the unit cell display a deficit of Na atoms, but a difference synthesis at the concluding stage of the interpretation revealed no appreciable maxima. The formula of arrojadite based on structural data can be written as



with  $Z = 8$ .

Fuchs<sup>2</sup> observed that arrojadite and panetite<sup>5)</sup> have similar composition and similar unit-cell parameters. According to Fuchs,<sup>2</sup> both minerals have defect structures which can be written in the form  $A_mB_n(PO_4)_{48}$ . The unit-cell contents of both minerals have variable amounts of cations A and B, the total positive charge on these being 144 approximately. In the light of this analogy, the statistical distribution of the cations over the X and A positions in the structure of arrojadite becomes perfectly normal.

The comparatively high value of the R-index may be due to the inexact proportion in which the cations are distributed over the X and A positions, and to the tendency of arrojadite to form polysynthetic twins owing to the ratio between the unit cell parameters,  $a \approx 16 \text{ \AA}$  and  $b \approx 24 \text{ \AA}$  (three times the  $a$  parameter is equal to twice the  $b$ ).

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<sup>1</sup>In a message to the mineralogical society of the USA, <sup>1</sup> Prof. D. Fisher, the first President of the International Mineralogical Association, mentions the large number (over 100) of phosphate minerals discovered mainly in pegmatites. In recent years this information has been supplemented by a number of discoveries of natural phosphates found not only in terrestrial rocks but also in meteorites (farringtonite, bryanite, panetite, etc.).<sup>2</sup>

<sup>2</sup>The crystal-geometrical characteristics of dickinsonite,  $(\text{Na}_2\text{K}_2\text{Ca}_3)(\text{Mn}_{39}\text{Fe}_{15}\text{Mg}_3)(\text{PO}_4)_{48}$  (Ref. 7), are:  $a = 24.89$ ;  $b = 10.11$ ;  $c = 16.68 \text{ \AA}$ ;  $\beta = 105^\circ 41'$ ;  $Z = 1$ ; space group  $C2/c$ .

<sup>3</sup>Motifs with condensed  $[\text{PO}_4]$  tetrahedra are less stable and are found only among synthetic compounds.<sup>10</sup>

<sup>4</sup>The slight excess of total negative charge in this formula can be compensated by oxidation of a small proportion of the Fe and Mn atoms to the trivalent state.

<sup>5</sup>The crystal geometry of panetite,  $(\text{Na}, \text{K})_{36}(\text{Mg}, \text{Ca}, \text{Fe}, \text{Mn})_6(\text{PO}_4)_{48}$  is as follows:  $a = 10.18$ ;  $b = 14.90$ ;  $c = 25.87 \text{ \AA}$ ;  $\beta \approx 91.1^\circ$ , Fedorov group  $P2_1/n$ . If we can find the structure of panetite, we should be able to answer the question of how it can be isostructural with arrojadite while their Fedorov groups are different.

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## Synthesis and crystal structure of double molybdates of sodium and zirconium

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The  $\text{Na}_2\text{MoO}_4\text{-Zr}(\text{MoO}_4)_2$  system has been found to contain double molybdates of the compositions  $\text{Na}_2\text{Zr}(\text{MoO}_4)_3$  (1:1) and  $\text{Na}_4\text{Zr}(\text{MoO}_4)_4$  (2:1). The compounds melt at 610 (1:1) and 625°C (2:1) with decomposition. Single crystals have been obtained from a solution in an  $\text{Na}_2\text{Mo}_2\text{O}_7$  melt. The crystal structures have been determined and refined by MLS from three-dimensional diffraction data (Weissenberg x-ray goniometer, Mo radiation) to  $R = 0.09$  and 0.092 (in the isotropic approximation). In the structure of  $\text{Na}_2\text{Zr}(\text{MoO}_4)_3$  the coordination polyhedra (Na and Zr eight-pointed polyhedra and Mo tetrahedra) and their linkages are like those for the scheelite structure. In the structure of  $\text{Na}_4\text{Zr}(\text{MoO}_4)_4$  the Zr and Mo atoms exhibit a similar coordination (8 and 4), but the coordination of the Na atoms is reduced to octahedral. The relation of both structures to the scheelite structure is discussed.

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Two series of double molybdates of sodium and tetravalent elements ( $\text{Me}^{4+} = \text{Th}, \text{Np}, \text{Pu}, \text{or } \text{U}$ ) of the compositions  $\text{Na}_2\text{Me}^{4+}(\text{MoO}_4)_3$  and  $\text{Na}_4\text{Me}^{4+}(\text{MoO}_4)_4$  have been obtained.<sup>1-5</sup> According to the x-ray data, all the compounds of the first series are isostructural with tetragonal scheelite, presupposing statistical distribution of the  $\text{Na}^+$

and  $\text{Me}^{4+}$  cations over the  $\text{Ca}^{2+}$  positions in the  $\text{CaWO}_4$  structure. Compounds of the second series also crystallize on the basis of the scheelite structure. We have investigated phase formation in the  $\text{Na}_2\text{MoO}_4\text{-Zr}(\text{MoO}_4)_2$  system, the conditions for synthesis of single crystals of the new phases in solutions in melts, and determined the