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The arrojadite enigma: I. A new formula and a new model for the arrojadite structure

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Abstract

A re-examination of the chemistry and structure of nearly all the known occurrences of arrojadite and related minerals (dickinsonite and sigismundite) allowed understanding of the main substitution vectors and cation ordering schemes ruling the crystal-chemistry of these very complex phosphates. Electron microprobe analyses were done with a careful choice of the standards and of experimental conditions, and were coupled with LA-ICP-MS in situ analysis for Li, Be, and B. Structure refinement was done in a space group (*Cc*) with a lower symmetry than those used in previous studies (*C*2/*c* and its equivalents), which allowed a better understanding of the structure details and of cation ordering. The combined approach yielded a new formula for the arrojadite group, namely $A_2B_2Ca_1Na_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$, where A are either large divalent cations (Ba, Sr, Pb) plus vacancy, or monovalent (K, Na) cations; and B are either small divalent cations (Fe, Mn, Mg) plus vacancy, or monovalent (Na) cations. The number of hydroxyl groups in the arrojadite formula is generally 3 apfu, and can be lowered to 2 apfu in particular when the sum of non-(P,Al) cations is higher than 20 apfu.

We present in this paper the complete characterization of three samples (two of which are new members) that are crucial to fix the cornerstones of arrojadite crystal-chemistry. The sample from Rapid Creek (Yukon Territory) is the holotype for arrojadite-(KNa), and has unit formula $K_{0.83}Na_{5.01}(Ca_{0.91}Sr_{0.01})_{\Sigma=0.92}(Fe^{2+}_{9.34}Mg_{2.69}Mn^{2+}_{1.03}Zn_{0.01}Li_{0.01})_{\Sigma=13.08}(Al_{1.04}Ti_{0.02})_{\Sigma=1.06}(OH_{1.97}F_{0.03})_{\Sigma=2.00}[(P_{11.99}Si_{0.01}T_1)O_{47}(OH)_{1.00}]$ [ideally, $^{A1}K\ ^{A2}Na\ ^{B1}Na\ ^{B2}Na\ ^{Na1,2}Na_2\ ^{Na3}\square\ ^{Ca}Ca\ ^{M}Fe_{13}\ Al\ (PO_4)_{11}\ ^{P1x}(PO_3OH)\ ^{W}(OH,F)_2$] and unit-cell dimensions: $a = 16.5220(11)$, $b = 10.0529(7)$, $c = 24.6477\ (16)$ Å, $\beta = 106.509(2)°$, $V = 3932.2(7)$ Å^3 ($Z = 4$). The sample from Horrsjöberg (Värmland, Sweden) is the holotype material for arrojadite-(SrFe), and has unit formula $Sr_{0.93}Na_{3.20}(Ca_{0.59}Ba_{0.20}Pb_{0.03}K_{0.03})_{\Sigma=0.85}(Fe^{2+}_{6.64}Mg_{3.61}Mn^{2+}_{3.33}Zn_{0.07}Li_{0.01})_{\Sigma=13.66}(Sc_{0.04}Al_{1.00})_{\Sigma=1.04}(OH_{1.10}F_{0.90})_{\Sigma=2.00}[(P_{11.95}Si_{0.02})_{\Sigma=11.97}O_{47}(OH)_{1.00}]$ [ideally, $^{A1}Sr\ ^{A2}\square\ ^{B1}Fe^{2+}\ ^{B2}\square\ ^{Na1,2}Na_2\ ^{Na3}\square\ ^{Ca}Ca\ ^{M}Fe^{2+}_{13}\ Al\ (PO_4)_{11}\ ^{P1x}(PO_3OH)\ ^{W}(OH,F)_2$], and unit-cell dimensions $a = 16.3992(7)$, $b = 9.9400(4)$, $c = 24.4434(11)$ Å, $\beta = 105.489(1)°$, $V = 3839.76(46)$ Å^3. The sample from Branchville (Connecticut) is the holotype material for dickinsonite-(KMnNa), and has unit formula $K_{0.50}Na_{5.78}(Ca_{0.51}Sr_{0.05}Ba_{0.01}Pb_{0.01})_{\Sigma=0.58}(Mn^{2+}_{9.70}Fe^{2+}_{3.72}Li_{0.31}Mg_{0.06}Zn_{0.01})_{\Sigma=13.80}(Al_{0.91}Fe^{3+}_{0.09}Ti_{0.01})_{\Sigma=1.00}(OH_{1.97}F_{0.03})_{\Sigma=2.00}[(P_{12.02}Si_{0.01})_{\Sigma=12.03}O_{47}(OH)_{0.21}]$ [ideally, $^{A1}K\ ^{A2}Na\ ^{B1}Mn\ ^{B2}\square\ ^{Na1,2}Na_2\ ^{Na3}Na\ ^{Ca}Ca\ ^{M}Mn_{13}\ Al\ (PO_4)_{11}\ ^{P1x}(PO_4)\ ^{W}(OH, F)_2$] and unit-cell dimensions $a = 16.6900\ (9)$, $b = 10.1013\ (5)$, $c = 24.8752\ (13)$ Å, $\beta = 105.616(2)°$, $V = 4038.9(7)$ Å^3.

Keywords: Crystal structure, arrojadite, analysis (chemical), new minerals, arrojadite-(KNa), arrojadite-(SrFe), dickinsonite-(KMnNa), optical properties, Raman spectroscopy, XRD data