

CRYSTAL STRUCTURE OF NEAR-ENDMEMBER ARROJADITE-(BaNa) FROM BIG FISH RIVER, YUKON, CANADA

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ABSTRACT

Arrojadite-(BaNa), $\text{BaNa}_3(\text{NaCa})\text{Fe}^{2+}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$, has been identified from Big Fish River, Yukon Territory, Canada. Arrojadite-(BaNa) was first discovered in the mine dumps of the Luna albite pegmatite, Dorio municipality, Lecco province, Italy (Vignola *et al.* 2016). At Big Fish River it is associated with apatite group minerals, gormanite, siderite, quartz, and other minerals in thin veins, phosphate nodules, and within the surrounding ironstone shales and mudstones of the Rapid Creek Formation. Arrojadite-(BaNa) occurs here as clear and colorless to slightly yellow or light-medium grey, ≤ 0.5 mm thick by 1 mm wide, tabular and platy crystals, as well as polycrystalline material. Zoning is visible in some tabular crystals, where the center of the crystal is medium grey in color and the edges appear clear and colorless. Differences exist in chemical composition and crystal structure between crystals from Big Fish River and the type specimen. In this paper, near-endmember arrojadite-(BaNa) from Big Fish River is presented with the empirical formula $\text{Ba}_{1.01}\text{Na}_{1.98}\text{Ca}_{0.82}\text{Na}_{2.0}(\text{Fe}^{2+}_{10.37}\text{Mg}_{2.06}\text{Mn}_{0.59})_{\Sigma 13.03}(\text{Al}_{1.10})(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_{2.00}$ [calculated using 12 P, 50 (O,OH,F) per formula unit]. According to the crystal structure model which refined to $R_1 = 5.4\%$, arrojadite-(BaNa) from Big Fish River is monoclinic, space group *Cc*, with unit cell dimensions a 16.5163(8) Å, b 10.0067(5) Å, c 24.5435(12) Å, β 106.121(2)°, V 3896.9(3) Å³, for $Z = 4$. Raman data showing clusters of bands in the OH-stretching region (3500–3600 cm⁻¹) suggest that the non-centrosymmetric space group *Cc* is correct for arrojadite-(BaNa) from Big Fish River. However, the arrojadite-(BaNa) specimen from the type locality, the Luna albite pegmatite, shows a single merged peak consistent with the centrosymmetric space group *C2/c* reported by Vignola *et al.* (2016).

Keywords: arrojadite-(BaNa), Arrojadite-group, Big Fish River, Yukon, single-crystal.

INTRODUCTION

Arrojadite-group minerals are complex phosphates which were originally identified in pegmatites and also occur in metamorphic and sedimentary environments (Headden 1891, Robertson 1982, Demartin *et al.* 1996). They are members of the arrojadite–dickinsonite–carmoite series, which includes nine International Mineralogical Association (IMA) approved mineral species. Cámara *et al.* (2006) and Chopin *et*

al. (2006) described a systematic chemical and structural investigation of arrojadite-group minerals that revamped the group. This new nomenclature (IMA CNMMN vote 05-D) has led to the definition, or re-definition, of several new members of this group based on dominant cations present at the dominant crystal-chemical sites and has provided a site nomenclature according to a new structural model in the non-centrosymmetric space group *Cc*. The structural formula proposed by Cámara *et al.* (2006) and

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Chopin *et al.* (2006) is $A_2B_2Ca_1Na_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$ where A represents large divalent cations (Ba, Sr, Pb) ($A1$) plus vacancy ($A2$) or two monovalent cations (K, Na) (both $A1$, $A2$) per formula unit (*pfu*); B is either two monovalent (Na) cations ($B1$ and $B2$) or small divalent cations (Fe, Mn, Mg) plus vacancy ($B1b,c$ and $B2$, respectively); M can include Fe, Mn, Mg, Zn, or Li; and W is OH or F. The dominant small divalent cation at the M site determines whether the root name is arrojadite (Fe), dickinsonite (Mn), or carmoite (Mg) (Cámara *et al.* 2006, 2015).

Vignola *et al.* (2016) described the first occurrence of arrojadite-(BaNa) in the Luna albite pegmatite of the Dorio municipality, Lecco Province, Italy. Arrojadite-(BaNa) occurs at that location as rounded masses or rough crystals up to 5 cm in diameter hosted by albite and frequently associated with fluorapatite (Vignola *et al.* 2016). The mineral has greasy luster and is pale greyish green to yellowish brown when altered. Good cleavage on {110} was observed (Vignola *et al.* 2016). Very recently, the fluorine-dominant endmember has been described by Števkó *et al.* (2018) from the dump of the Elisabeth adit near Gemerská Poloma village, Rožňava County, Košice Region, Slovak Republic.

Vignola *et al.* (2016) calculated the empirical formula on the basis of 12 P and 2 (OH, F) atoms per formula unit (*apfu*) as $(Ba_{0.62}K_{0.27}Pb_{0.13}Sr_{0.07})_{\Sigma 1.09}Na_3(Na_{1.19}Ca_{0.85})_{\Sigma 2.04}(Fe^{2+}_{9.82}Mg_{1.92}Mn^{2+}_{1.64})_{\Sigma 13.38}Al_{1.01}(PO_4)_{11}(HPO_4)(OH_{1.75}F_{0.25})_{\Sigma 2.00}$, with a simplified formula of $BaNa_3(NaCa)Fe^{2+}_{13}Al(PO_4)_{11}(PO_3OH)OH_2$. The unit-cell parameters for the mineral were obtained from single-crystal diffraction data and were determined to be monoclinic a 16.4984(6) Å, b 10.0228(3) Å, c 24.648(1) Å, β 105.850(4)°, and V 3920.8(2) Å³ for $Z = 4$ (Vignola *et al.* 2016). The structure was refined in the $C2/c$ space group.

Arrojadite-(BaNa) from Big Fish River (BFR) occurs within the Rapid Creek Formation, representing the first occurrence of this mineral in epithermal veins within a sedimentary environment. At BFR the Rapid Creek Formation is 60 m thick and consists of intercalated thin to medium beds of phosphatic ironstone and iron-rich dark grey shales (Young & Robertson 1984, Robinson *et al.* 1992). In the ironstone facies of the Rapid Creek Formation phosphate grains consist of apatite/"francolite", arrojadite-group minerals, satterlyite, and gormanite, the latter two being first described from this location (Robertson 1982, Young & Robertson 1984). The type specimen of arrojadite-(KNa) is from Rapid Creek, Yukon, less than 20 km from BFR and also within the Rapid Creek Formation. Robinson *et al.* (1992)

reported Ba-zoning in arrojadite-group minerals at Rapid Creek and BFR, as well as chemical compositions with significant amounts of F or Fe^{3+} , indicating the potential for new endmembers to be identified.

In this study, arrojadite-(BaNa) crystals were studied crystallochemically, with two crystals (W1 n.1 and W1 n.5) from sample W1 chosen for the full description reported here. These crystals were chosen due to their near-endmember chemistry and close fit between chemistry and site assignments from crystal structure refinement. Here we present a full description of arrojadite-(BaNa) from BFR and compare these low-temperature arrojadite-(BaNa) samples to the first occurrence.

GEOLOGICAL BACKGROUND AND SAMPLE DESCRIPTION

The BFR area lies within the Richardson Mountains of the northeastern Yukon, Canada, near the border with the Northwest Territories at approximate longitude 68° 28' N, latitude 136° 28' W (Fig. 1). There are 46 phosphate minerals identified as occurring at this locality, and BFR is the type locality for the minerals barićite (Sturman & Mandarino 1976), gormanite (Sturman *et al.* 1981a), marićite (Sturman *et al.* 1977), nahpoite (Coleman & Robertson 1981), satterlyite (Mandarino *et al.* 1978), and wicksite (Sturman *et al.* 1981b).

The Rapid Creek Formation was deposited as part of an Aptian-Albian flyschoid sequence in the Blow trough, an early- to mid-Cretaceous north-south structural depression about 50 km wide extending southward from the Beaufort-Mackenzie Basin (Young & Robertson 1984, Robinson *et al.* 1992). The sequence was bordered by the Cache Creek High to the east, where the Richardson Mountains are now located, and uplift to the west (Young & Robertson 1984, Robinson *et al.* 1992). This uplift and the subsidence of the Blow trough resulted in the formation of a thick sequence of turbidite sandstone, conglomerates, mudstones, and shales which thin towards the eastern structural high and grade into the iron-rich shales and phosphatic ironstones of the Rapid Creek Formation (Young & Robertson 1984, Robinson *et al.* 1992). The Rapid Creek Formation thins from 1000 to 60 m in the BFR area, where it is overlain by the Upper Cretaceous shales of the Boundary Creek Formation and underlain by Lower Cretaceous concretionary shales and sandstones of the Rat River Formation (Young & Robertson 1984, Robinson *et al.* 1992).

Arrojadite-group minerals, satterlyite, gormanite, and apatite/"francolite" comprise the primary phosphate grains within the ironstone facies of the Rapid Creek Formation (Robertson 1982, Young &

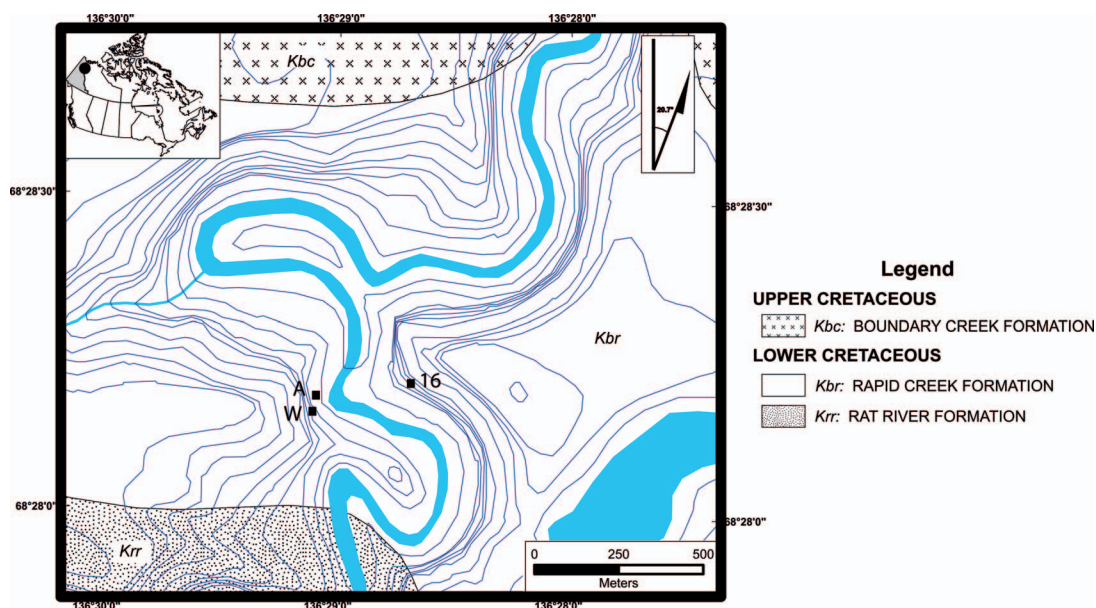


FIG. 1. Map of the Big Fish River Area, Yukon. Sites A and W are from this study; Site 16 is from Robinson *et al.* (1992). Note: 50 m contour spacing.

Robertson 1984). According to Robertson (1982), the sediments originally contained an unknown Ca-Fe-Mg phosphate or apatite plus unidentified Fe-Mg phosphate mineral, which together with remobilized siderite from the host sandstones was altered to these unusual phosphates during very low-grade metamorphism. In the mudstones the unknown phosphate mineral was altered to carbonate-apatite, occurring with siderite, as well as gormanite-souzalite alteration and replacement (Robertson 1982). Previous studies found no evidence for high-temperature crystallization of the minerals within the Rapid Creek Formation. Robertson (1982) reported preliminary results for temperature of formation as $\sim 50^\circ\text{C}$ for vein siderite and quartz, obtained from oxygen isotope geochemistry and using a geothermal gradient based on overlying strata of 2300 m thickness. Preliminary fluid inclusion studies by Robinson *et al.* (1992) on lazulite and quartz veins at Rapid Creek yielded minimum temperatures of $180\text{--}200^\circ\text{C}$, and the authors noted that the pressure conditions were unknown due to the uncertainty of the age of the phosphate-quartz veins in relation to the overlying sediments. Studies are currently underway by one of the authors (HT) to further understand the thermodynamic and geochemical factors controlling the formation of the phosphate minerals in the Rapid Creek Formation, which is expected to improve our understanding of how these, and analogous mineral phases, can naturally occur.

The arrojadite-group minerals and quartz precipitated early in the paragenetic sequence, under unknown *P-T* conditions, from low-salinity fluids during or after the Laramide orogeny, which created the fractures where the fluid precipitated (Robertson 1982, Robinson *et al.* 1992). The arrojadite-group minerals are part of an Fe-Mg-rich association occurring in siderite-rich sandstones at Rapid Creek where the abundance of siderite in the host rocks combined with Na-bearing fluids form arrojadites and other Fe-rich phosphate minerals (Table 1; Robertson 1982). There are no typical assemblages within the Fe-Mg-rich association, and veins of only arrojadite-group minerals are common (Robertson 1982).

The lower portion of the Rapid Creek Formation at BFR (locality 16, Fig. 1) contains pyrite and phosphate nodules that host a variety of rare phosphate minerals (Robertson 1982, Young & Robertson 1984, Robinson *et al.* 1992). Arrojadite-group minerals co-exist with wolfeite, satterlyite, pyrite, maričite, and wicksite in these nodules (Robertson 1982, Young & Robertson 1984, Robinson *et al.* 1992).

At BFR, arrojadite-(BaNa) occurs in veins commonly with quartz and occasionally vivianite-baričite (Robertson 1982). Other minerals associated with the veins include arrojadite-(KNa), members of the apatite group, collinsite, kryzhanovskite, metavivianite, whitlockite, and whiteite-(CaFeMg). Other veins contain millimeter-sized crystals of arrojadite-(BaNa) in

TABLE 1. THE FORMULAE OF THE PHOSPHATE MINERALS ASSOCIATED WITH ARROJADITE-GROUP MINERALS IN THE RAPID CREEK FORMATION, YUKON

Mineral	Chemical Formula
Apatite group	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$
Arrojadite-(BaNa)	$\text{BaNa}_3(\text{NaCa})\text{Fe}^{2+}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$
Arrojadite-(KNa)	$\text{KNa}_3(\text{CaNa}_2)\text{Fe}^{2+}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$
Augelite	$\text{Al}_2(\text{PO}_4)(\text{OH})_3$
Barićite	$(\text{Mg}, \text{Fe})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
Collinsite	$\text{Ca}_2\text{Mg}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
Gormanite	$\text{Fe}^{2+}_3\text{Al}_4(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$
Kryzhanovskite	$(\text{Fe}^{3+}, \text{Mn}^{2+})_3(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_3$
Kulanite	$\text{BaFe}^{2+}_2\text{Al}_2(\text{PO}_4)_3(\text{OH})_3$
Marićite	$\text{NaFe}^{2+}(\text{PO}_4)$
Metavivianite	$\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$
Satterlyite	$(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_{12}(\text{PO}_3\text{OH})(\text{PO}_4)_5(\text{OH}, \text{O})_6$
Souzalite	$\text{Mg}_3\text{Al}_4(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$
Vivianite	$\text{Fe}^{2+}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$
Whiteite-(CaFeMg)	$\text{CaFe}^{2+}\text{Mg}_2\text{Al}_2(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$
Whitlockite	$\text{Ca}_3\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$
Wicksite	$\text{NaCa}_2\text{Fe}^{2+}_2(\text{Fe}^{3+}, \text{Mn}^{2+}, \text{Fe}^{2+})_4(\text{PO}_4)_6 \cdot 2\text{H}_2\text{O}$
Wolfeite	$\text{Fe}^{2+}_2(\text{PO}_4)(\text{OH})$

association with siderite, gormanite, augelite, and quartz. Within the matrix and phosphate nodules arrojadite-(BaNa) is associated with gormanite-souzalite, satterlyite, apatite/"francolite", siderite, quartz, and pyrite. Associated mineral formulae are shown in Table 1.

Much of the material analyzed for this study was collected from well-crystallized veins located along faults amongst the cliffs at Big Fish River (sites W and A, Fig. 1). Sample W1 (containing crystals W1 n.1 and W1 n.5) was collected from an east-west trending faulted arrojadite-(BaNa) vein, 4 cm wide and hosting mm-sized crystals, located high on a ridge.

Arrojadite-(BaNa) from BFR forms as ≤ 0.5 mm thick by 1 mm wide tabular and platy crystals in open veins (Fig. 2). The crystals are often clear and colorless, slightly yellow or light to medium grey, transparent to translucent with a white streak and vitreous luster. Zoning is visible in some of the tabular crystals where the center is medium grey and the edges appear clear and colorless (sample W1; Fig. 2). Light grey to slightly green polycrystalline arrojadite-(BaNa) filled veins occur from less than 1 mm up to 4 cm wide, with open pockets up to 1 cm wide. The calculated density is 3.620 g/cm^3 for colorless crystals and 3.710 g/cm^3 for grey crystals from sample W1.

CHEMICAL COMPOSITIONS

Quantitative chemical compositions were obtained from crystal fragments of arrojadite-(BaNa) in polished and carbon-coated mounts at Queen's

University, Kingston, Canada, with a wavelength dispersive JEOL JXA-8230 electron microprobe instrument (EMPA) operating at 15 kV and 20 nA beam current with a 10 μm spot size. The standards used were albite ($\text{AlK}\alpha$, $\text{NaK}\alpha$), synthetic fluorophlogopite ($\text{FK}\alpha$), synthetic $\text{Ca}_2\text{P}_2\text{O}_7$ ($\text{PK}\alpha$), synthetic diopside ($\text{CaK}\alpha$, $\text{MgK}\alpha$, $\text{SiK}\alpha$), hematite ($\text{FeK}\alpha$), rhodonite Harvard 104791 ($\text{MnK}\alpha$), rutile NMNH 120812 ($\text{TiK}\alpha$), orthoclase ($\text{KK}\alpha$), gahnite NMNH 145883 ($\text{ZnK}\alpha$), strontianite NMNH R10065 ($\text{SrL}\alpha$), sanbornite ROM M17022 ($\text{BaL}\beta$), and cerussite



Fig. 2. Crystal of arrojadite-(BaNa), specimen W1 (in circle). The clear, colorless (W1 n.5) zones are visible along the edges, and the center of the crystal is medium grey (W1 n.1). White augelite crystals and green gormanite needles are associated with arrojadite-(BaNa) on the specimen.

(PbM α). Data were corrected using atomic number and absorption corrections from Pouchou & Pichoir (1991) in combination with the mass absorption coefficients of Heinrich (1987). The characteristic fluorescence correction of Reed (1990) and the continuum fluorescence correction from Springer (1971) were also applied. Precision and detection limits were calculated according to expressions given by Williams (1987). Results for F, Pb, Si, Sr, Ti, Zn, and element values of (–) were at or below detection limits in these samples.

The chemical compositions of the crystals analyzed are in Table 2, based on average values obtained from 20 and 14 spots per crystal. The empirical formula was calculated using 12 P, 50 (O+OH+F), using the method outlined by Chopin *et al.* (2006). In this study, the site nomenclature of Chopin *et al.* (2006) is used and the corresponding site nomenclature used by Vignola *et al.* (2016) is indicated in brackets throughout the text. Where required, Fe³⁺ was calculated based on excess FeO and a deficiency of Al³⁺ to fill the remainder of the Al³⁺ site and resolve charge balance issues. High Ba at the A1 (= X5) site, combined with low Mn and Mg, and high Fe²⁺ indicate that sample W1 corresponds closely to near-endmember arrojadite-(BaNa). The colorless zone (W1 n.5) is the closest composition to endmember arrojadite-(BaNa) with the empirical formula Ba_{1.01}Na_{1.98}Ca_{0.82}Na_{2.0}(Fe²⁺_{10.37}Mg_{2.06}Mn_{0.59}) Σ _{13.03}(Al_{1.10})(PO₄)₁₁(PO₃OH)(OH)_{2.00}. Crystal fragment W1 n.1, from the medium grey region in the zoned crystals of W1 (Fig. 2), containing Fe³⁺, has the empirical formula Ba_{1.01}(Na_{1.83}K_{0.05})Ca_{1.02}Na_{2.0}(Fe²⁺_{10.66}Mg_{1.79}Mn_{0.57}) Σ _{13.03}(Al_{0.80}Fe³⁺_{0.20}) Σ _{1.0}(PO₄)₁₁(PO₃OH)(OH)_{2.00}.

X-RAY DIFFRACTION AND CRYSTAL STRUCTURE DETERMINATION

Powder X-ray diffraction (PXRD) data were obtained with a Bruker D8 Advance diffractometer system using a two-circle goniometer setup at the Royal Ontario Museum in Toronto, Canada. The pattern was recorded at 40 kV, 40 mA, 5–105° 2 θ , 0.01 step increments, 10 s per step, and Cu radiation (λ CuK α 1 = 1.54059 Å). The data were collected using coupled 2 θ / θ , Göbel mirror, 0.6 mm physical slit, air scatter screen, 5.5 mm secondary motorized slit, and a LynxEye detector with opening 2.9 and lower discriminator of 0.19. A low-background plate made of silicon crystal was set to 5 rotations/min. Powder XRD was collected from a mix of zoned colorless and grey crystals taken from the same pocket in sample W1. A mixed sample was used due to the small grain size, consistent zoning, and few crystals available.

Refinement of unit-cell parameters and indexing of Bragg reflections were performed using GSAS-II (Toby & Von Dreele 2013). Observed and calculated spacings and intensities are reported in Table 3. The refined unit cell parameters for space group *Cc* are *a* 16.543(10) Å, *b* 10.069(1) Å, *c* 24.637(23) Å, β 106.00(3)°, *V* 3945.0(14) Å³, for *Z* = 4.

Single crystal X-ray diffraction data were collected (Table 4) at the CNR Instituto di Geoscienze e Georisorse (IGG), unità di Pavia, Pavia, Italy. The data were collected with a Bruker/AXS SMART Apex diffractometer equipped with graphite-monochromatized MoK α radiation. Ten batches of 900 images were collected at multiple ϕ positions and at two different θ -arm positions (θ = 20°: 0, 90, 180, 270; θ = 50°: 0, 45, 90, 135, 180, 270). The data were collected with a frame width of 0.2 in ω , a crystal-to-detector distance of 8 cm, and with a 5 s counting time per frame. The SAINT program (Bruker 2003) was used to integrate the intensity data and the SADABS program was used for absorption corrections (Sheldrick 2015). All crystal structures were refined using SHELXL97 (Sheldrick 2015) in the monoclinic *Cc* space group recommended by Cámara *et al.* (2006). Because the $|E^2 - 1|$ statistics yielded a value of 0.936, closer to the value expected for a centric structure, data were also tested with a *C2/c* model starting from the atom coordinates reported by Vignola *et al.* (2016) and a *A2/a* model starting from the coordinates of arrojadite-(KFe) from Nancy Mine, NH, USA, reported by Moore *et al.* (1981). In both cases the agreement factors were worse than for the *Cc* model, yielding for crystal fragment W1 n.1 *R*1 = 0.0802 for 8307 *F*_o > 4 σ (*F*_o) and 0.0822 for all 8609 data (*C2/c* model) and *R*1 = 0.0793 for 8307 *F*_o > 4 σ (*F*_o) and 0.0813 for all 8609 data (*A2/a* model) and for crystal fragment W1 n.5 *R*1 = 0.0852 for 8206 *F*_o > 4 σ (*F*_o) and 0.0877 for all 8581 data (*C2/c* model) and *R*1 = 0.0844 for 8207 *F*_o > 4 σ (*F*_o) and 0.0869 for all 8582 data (*A2/a* model) (compare with the lower *R*1 values reported in Table 4). The *Cc* model did not yield any negative anisotropic displacement parameters. The $|E^2 - 1|$ value may not be reliable when heavy atoms are located at special positions, like Ba in this mineral. Refinement with the *Cc* model showed the presence of twinning by the missing diad (–1 0 0, 0 1 0, 0 0 –1) of 37(2)% and a 6(1)% for crystal fragments W1 n.1 and W1 n.5, respectively. This twinning is not recognizable in the reciprocal space, as nodes of both orientations are perfectly superimposed.

Our single-crystal data show, therefore, that near-endmember arrojadite-(BaNa) from BFR (crystal fragment W1 n.5) is better described with a monoclinic *Cc* model, with *a* 16.5163(8) Å, *b* 10.0067(5) Å, *c* 24.5435(12) Å, β 106.121(2)°, *V* 3896.9(3) Å³, for *Z*

TABLE 2. ELECTRON MICROPROBE ANALYSES AND STOICHIOMETRY FOR ARROJADITE-(BaNa) SAMPLES

	W1 n.1		W1 n.5		Average Luna Pegmatite ¹	
	Mean (20)		Mean (14)		Mean (20)	
	wt.%	e.s.d.	wt.%	e.s.d.	wt.%	e.s.d.
P ₂ O ₅ *	39.42		39.84		39.73	(0.45)
Al ₂ O ₃	1.88	(0.12)	2.61	(0.26)	2.4	(0.06)
Fe ₂ O ₃ *	0.75					
FeO	35.45*		34.87	(0.88)	32.91	(0.28)
MnO	1.88	(0.08)	1.97	(0.23)	5.41	(0.12)
MgO	3.35	(0.15)	3.89	(0.42)	3.6	(0.11)
BaO	7.19	(0.09)	7.27	(0.10)	4.43	(0.25)
Na ₂ O	5.49	(0.10)	5.77	(0.10)	6.06	(0.13)
K ₂ O	0.10	(0.02)	—	—	0.59	(0.04)
CaO	2.66	(0.07)	2.16	(0.15)	2.22	(0.18)
SrO	—	—	—	—	0.35	(0.08)
PbO	—	—	—	—	1.35	(0.12)
F	—	—	—	—	0.22	(0.05)
H ₂ O**	1.25		1.26		1.12	
TOTAL	99.42		99.63		100.39	
—O=F	0.00		0.00		—0.09	
TOTAL	99.42		99.63		100.30	
P ₂ O ₅ (or.)	39.54	(0.23)	39.59	(0.37)		
FeO total	36.12	(0.32)				
P	12.000		12.000		12.000	
Al	0.798		1.095		1.010	
Fe ³⁺	0.202					
Fe ²⁺	10.660		10.374		9.820	
Mn ²⁺	0.572		0.592		1.636	
Mg	1.793		2.064		1.916	
ΣM	13.025		13.031		13.372	
Ba	1.013		1.013		0.620	
Na	3.826		3.979		4.190	
K	0.048		—		0.268	
Ca	1.024		0.823		0.849	
Sr	—		—		0.072	
Pb	—		—		0.130	
ΣX	5.911		5.815		6.129	
F	—		—		0.247	
OH	3.000		3.000		1.753	
ΣOH + F	3.000		3.000		2.000	

Note: F, Pb, Si, Sr, Ti, Zn, and K (in W1 n.5) were below detection limit; A “—” indicates analyses at or below detection limit.

* Calculated values; original P₂O₅ and FeO total are reported after the total row. Original P₂O₅ modified to obtain 12 P *pfu* in stoichiometric calculation with 47 O and 3 (OH + F) *pfu* following the procedure in Chopin *et al.* (2006); Fe³⁺ calculated using excess FeO to fill the deficiency of Al³⁺ in the Al site and resolve charge balance issues for sample W1 n.1.

** Calculated to obtain 3 (OH + F) *pfu*.

¹ Vignola *et al.* (2016).

TABLE 3. A LIST OF THE POWDER DIFFRACTION d -SPACINGS AND INTENSITIES FOR ARROJADITE-(BaNa) FROM BIG FISH RIVER

hkl	d_{obs}	d_{calc}	h	k	l	hkl	d_{obs}	d_{calc}	h	k	l
6	8.5279	8.5083	1	1	0	3	2.3482	2.3472	5	3	3
7	7.6759	7.6593	2	0	2	3	2.3033	2.3026	7	1	3
10	7.4612	7.4541	1	1	2	3	2.2634	2.2628	5	3	5
11	5.9104	5.9229	0	0	4	6	2.2175	2.2171	2	4	5
5	5.5360	5.5437	2	0	4	19	2.1948	2.1951	5	3	6
6	5.2389	5.2390	1	1	4	5	2.1418	2.1437	0	2	10
7	5.0034	5.0347	0	2	0	7	2.1135	2.1139	1	3	9
9	4.7813	4.7824	3	1	2	2	2.0780	2.0797	7	1	2
9	4.6928	4.6920	3	1	0	3	2.0518	2.0540	2	0	12
18	4.6365	4.6336	0	2	2	3	2.0137	2.0140	6	2	9
13	4.5552	4.5546	1	1	4	4	1.9965	1.9967	1	5	1
3	4.2548	4.2542	2	2	0	11	1.9863	1.9862	4	2	11
12	4.2038	4.2072	2	2	2	10	1.9802	1.9814	1	5	2
3	4.0348	4.0363	3	1	2	11	1.9443	1.9549	2	4	8
2	3.9505	3.9486	0	0	6	18	1.9096	1.9109	7	3	1
6	3.8307	3.8297	4	0	4	2	1.8777	1.8779	8	0	2
6	3.4674	3.4695	3	1	6	7	1.8563	1.8583	6	4	3
17	3.3904	3.3946	1	1	6	4	1.8441	1.8428	7	3	1
13	3.3044	3.3043	3	1	4	2	1.8270	1.8272	7	1	5
7	3.2356	3.2352	2	2	4	2	1.7797	1.7829	9	1	6
47	3.2019	3.2009	2	0	6	12	1.7536	1.7546	6	4	2
9	3.1221	3.1218	5	1	3	8	1.7444	1.7446	6	0	13
100	3.0401	3.0338	5	1	0	3	1.7019	1.7017	5	5	0
7	2.9595	2.9615	0	0	8	2	1.6821	1.6829	5	5	5
7	2.9371	2.9353	1	1	8	4	1.6606	1.6600	7	1	7
15	2.8546	2.8557	3	3	2	7	1.6463	1.6452	4	2	14
24	2.8339	2.8361	3	3	0	2	1.6317	1.6317	2	6	1
11	2.8046	2.8048	3	3	3	3	1.6118	1.6114	9	3	3
27	2.7572	2.7577	4	2	6	8	1.6005	1.6005	4	0	12
30	2.6993	2.6998	4	0	5	9	1.5594	1.5596	2	6	4
5	2.6650	2.6699	3	3	2	5	1.5238	1.5240	8	4	8
3	2.6125	2.6104	5	1	3	5	1.4859	1.4863	2	6	6
7	2.5959	2.5992	1	3	6	3	1.4661	1.4657	2	4	12
5	2.5796	2.5820	3	1	9	2	1.4541	1.4548	11	1	8
35	2.5448	2.5436	4	0	9	4	1.4335	1.4335	11	1	9
13	2.5168	2.5173	0	4	0	5	1.4281	1.4281	9	3	4
14	2.5102	2.5033	0	4	1	8	1.4143	1.4139	2	2	15
9	2.4154	2.4157	1	1	9	3	1.3848	1.3846	1	7	4
7	2.3857	2.3912	6	2	4	3	1.3582	1.3581	9	5	4

The 10 most intense reflections recorded in this study are in bold.

= 4. The data were refined to $R_1 = 0.054$ based on a total of 43404 measured reflections; of these, 15443 were unique and 14460 observed using the criterion $[I_{\text{obs}} > 2\sigma(I)]$. The crystal model for near-endmember arrojadite-(BaNa) is shown in Figure 3. The starting model was arrojadite-(KNa) from Cámara *et al.* (2006) and using the same site nomenclature approved by IMA CNMMN (vote 05-D), the atomic coordinates and anisotropic displacement factors were refined for all atoms except site A2 due to its very low site occupancy. We used fully ionized scattering factors

for cation sites and neutral scattering factors for oxygen atoms, except for sites O2a and O25b, for which a half-ionized curve for O was used to account for hydroxyl groups. Scattering curves for neutral and ionized atoms, together with anomalous dispersion corrections, were taken from the International Tables for X-ray Crystallography (Wilson 1992). The site scattering of all cation sites except the *P* sites was refined to allow for the substitution of Ba at the A1 site, the diverse Fe content at the *M* sites, the possible presence of Fe^{3+} at the *Al* site, and the occupancy of

TABLE 4. SUMMARY OF CRYSTALLOGRAPHIC DATA AND REFINEMENT RESULTS FOR THE STUDIED ARROJADITE-(BaNa) CRYSTALS

	W1 n.1	W1 n.5
Crystal System	Monoclinic	Monoclinic
Space Group	<i>Cc</i>	<i>Cc</i>
<i>a</i> (Å)	16.5335 (10)	16.5163 (8)
<i>b</i> (Å)	10.0225 (6)	10.0067 (5)
<i>c</i> (Å)	24.5827 (15)	24.5435 (12)
β (°)	106.123 (2)	106.121 (2)
<i>V</i> (Å ³)	3913.3 (4)	3896.9 (3)
<i>Z</i>	4	4
No. of reflections collected	43776	44573
No. of independent reflections	16816	15423
No. of reflections with $I > 2\sigma(I)$	15748	14443
R_{int}	0.037	0.027
$R1 [F_o > 4\sigma(F_o)]$	0.057	0.055
$wR2$	0.148	0.137
R_{all}	0.059	0.058
$wR2$ all	0.150	0.140
Goodness-of-fit	1.05	1.03
No. of parameters refined	829	836

the *Ca*, *Na1*, *Na2*, *B1*, and *B2* sites. Table 4 contains selected crystal and refinement data for the analyzed arrojadite-(BaNa) crystals. Table 5 reports mean bond-lengths for cation sites and refined O–H distances (when H was observed in the Fourier-difference maps and added to the model; some are unrealistically short due to the difficulty of refining the proton position in this material). Table 6 reports observed site scattering for cation site comparison of aggregate values for *M* and *Ca*, *Na*(1,2), *A*(1,2), and *B*(1,2) sites obtained by refinement and EMPA analyses. Atom coordinates and anisotropic displacement parameters (CIF) and observed and calculated structure factors are available from the Depository of Unpublished Data on the MAC website [document Arrojadite-(BaNa) CM56_10.3749/canmin.1800018].

RAMAN SPECTROSCOPY

Raman spectra were obtained from unoriented crystal fragments mounted in epoxy for microprobe analysis. A Horiba LabRAM ARAMIS fully automated confocal Raman microscope was used at the Royal Ontario Museum, Toronto, Canada. A 532 nm polarized laser at 25 mW was used with spot sizes of 791 and 1298 nm, a 1200 groove density grating, 200

μm confocal hole, and 150 μm slit. The instrument was calibrated using a Si metal wafer.

The Raman spectra of arrojadite-(BaNa) from sample W1 n.5 is plotted in Figure 4 and shows bands in the 420–450 cm^{−1} (ν_2 PO₄ and H₂PO₄ bending modes), 530–590 cm^{−1} (ν_4 out-of-plane bending modes of the PO₄ and H₂PO₄ units), and 630–720 cm^{−1} regions, as well as a sharp shoulder at 920 cm^{−1} on the edge of the strongest band (PO₄³⁺ ν_1 symmetric stretching modes). The strongest band is in the 960–1030 cm^{−1} range and is attributed to ν_3 antisymmetric stretching of the PO₄ groups (Frost *et al.* 2013).

The OH-stretching region, shown in Figure 5, has two clusters of bands in the 3500–3600 cm^{−1} range, with local maxima at 3526 and 3555 cm^{−1}. The two distinct clusters of bands in this region strongly support the contention that the non-centrosymmetric space group *Cc* is correct for arrojadite-(BaNa) from BFR and correlates with findings by Cámara *et al.* (2006) from analyzing other arrojadite group end-members. In *C2/c* symmetry the *W* sites, which in the samples presented here contain only (OH) groups, would merge into one site (Cámara *et al.* 2006), therefore the two bands visible here represent the (OH) group at the *W1* and *W2* sites of the crystal structure.

It is noteworthy that no bands have been observed at 1460–1500 cm^{−1}. Using Fourier-transform infrared spectroscopy (FTIR) Della Ventura *et al.* (2014) analyzed arrojadite-(KNa) from Rapid Creek, Yukon (sample RC41081) and found two relatively sharp peaks overlapping a broad band at 3188 and 3087 cm^{−1}, respectively, coupled with an intense and strongly polarized doublet at 1458 and 1434 cm^{−1}. Della Ventura *et al.* (2014) interpreted the doublet at 1458 and 1434 cm^{−1} as vibration of the N–H bond in an NH₄⁺ molecule (the presence of N was also confirmed by EMPA), while the peaks at *ca.* 3200 cm^{−1} were due to the proton bonded to the *O3x* site, *i.e.*, *OH3* (see Cámara *et al.* 2006 for site nomenclature and hydrogen local environments). Whereas Della Ventura *et al.* (2014) did not propose any structural location for the NH₄⁺ molecule, it would seem plausible that it substitutes for the proton at the *OH3* site, occupying the *Na3* site, as does the Na in dickinsonite-(KMnNa) (Cámara *et al.* 2006). A broad band at *ca.* 3200 cm^{−1} was also observed in arrojadite-(KFe) from the Nickel Plate mine (South Dakota) by Della Ventura *et al.* (2014). It is interesting to note that in the Ba-rich arrojadite studied here there are no indications of the presence of NH₄⁺ and the peaks or broadband corresponding to *OH3* protons are not evident. As no electron density has been observed at the *Na3* site, it seems probable that the absence of the bands at *ca.* 3200 cm^{−1} are due to polarization effects

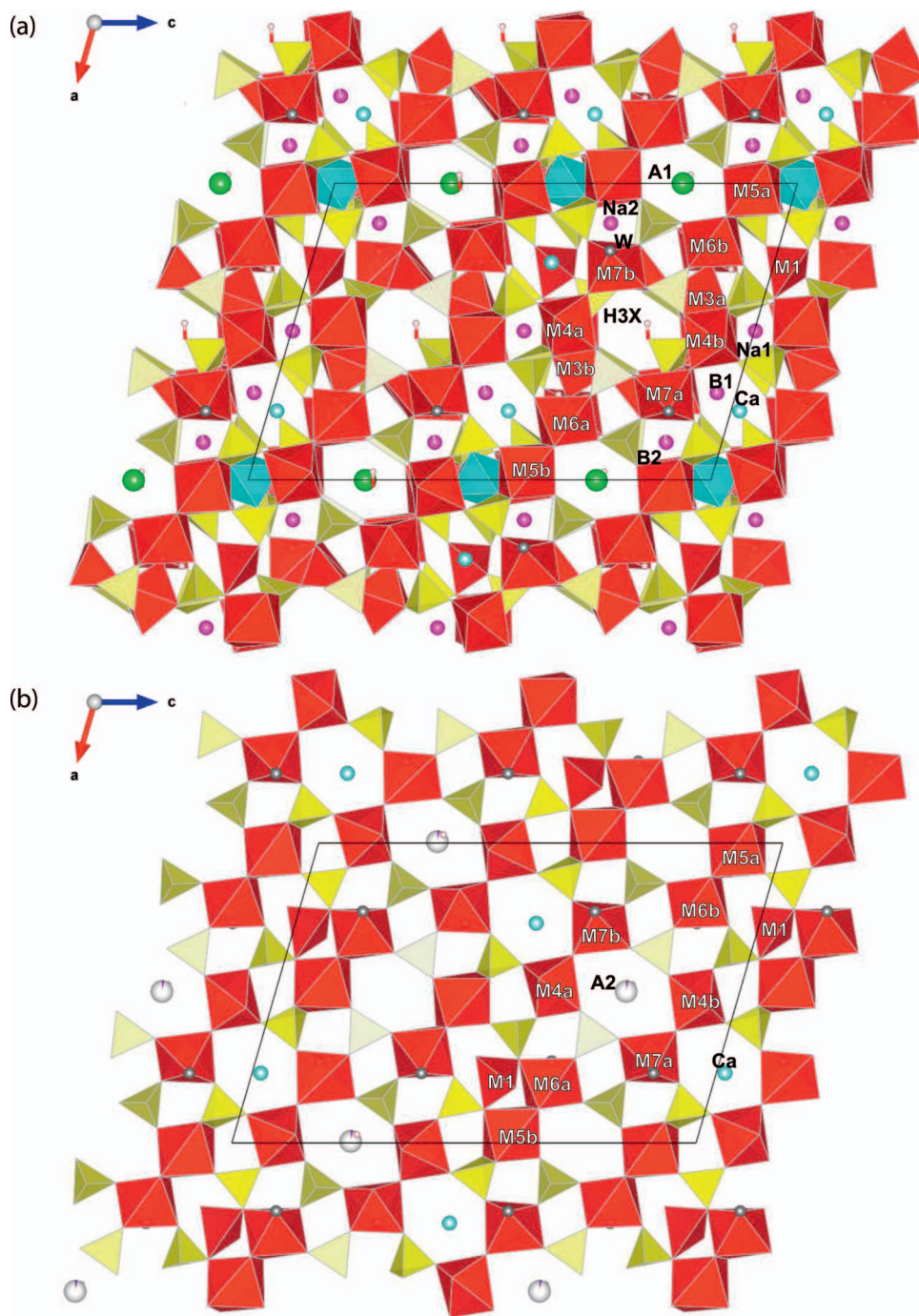


FIG. 3. The crystal structure of arrojadite-(BaNa) sample W1 n.5 projected along (010) at (A) $y = \frac{1}{2}$ and (B) $y = \frac{1}{4}$. Yellow tetrahedra = PO_4 ; blue octahedra = Al^{3+} (Al sites); red polyhedra = Fe^{2+} , Mg^{2+} , or Mn^{2+} (M sites); green spheres = Ba (A1 sites); purple spheres = Na (B1, B2, Na1, Na2 sites); light blue spheres = Ca (Ca sites); white spheres = K (A2 sites); and grey spheres = O25A and O25B (W sites). Figure drawn with Vesta 3.0 (Momma & Izumi 2011).

TABLE 5. MEAN BOND LENGTHS (IN Å) FOR CATION SITES IN THE STUDIED ARROJADITE-(BaNa) CRYSTALS

Site/sample	W1 n.1	W1 n.5
<P1–O>	1.538	1.537
<P1x–O>	1.538	1.535
<P2a–O>	1.541	1.537
<P2b–O>	1.535	1.538
<P3a–O>	1.539	1.537
<P3b–O>	1.536	1.534
<P4a–O>	1.537	1.539
<P4b–O>	1.532	1.532
<P5a–O>	1.537	1.531
<P5b–O>	1.536	1.541
<P6a–O>	1.536	1.539
<P6b–O>	1.540	1.540
<Al–O>	1.898	1.881
< ^{VI} M1–O>	2.135	2.135
< ^{IV} M1–O>	2.030	2.031
<M2a–O>	2.108	2.107
<M2b–O>	2.078	2.077
<M3a–O>	2.111	2.106
<M3b–O>	2.114	2.108
<M4a–O>	2.135	2.134
<M4b–O>	2.123	2.120
<M5a–O>	2.148	2.150
<M5b–O>	2.159	2.160
<M6a–O>	2.203	2.199
<M6b–O>	2.196	2.201
<M7a–O>	2.164	2.157
<M7b–O>	2.201	2.199
<Ca–O>	2.478	2.466
<A1–O>	2.855	2.848
<A2–O>	2.943	2.893
< ^{VI} B1–O>	2.575	2.786
< ^{IV} B1–O>	2.302	2.331
<B2–O>	2.541	2.537
<Na1–O>	2.575	2.550
<Na2–O>	2.564	2.567
O25a–H1		1.01(10)
O25b–H2		0.54(11)
O3x–H3	0.85(11)	0.87(11)

(see Della Ventura *et al.* 2014). Moreover, Frost *et al.* (2013) also reported a Raman-FTIR study of arrojadite-(KFe) from Rapid Creek (Yukon) and described a doublet at 1455 and 1431 cm^{-1} and a broad band at 3200 cm^{-1} in an FTIR spectrum. Although a doublet was also observed at 1426 and 1575 cm^{-1} in the Raman spectrum of the same sample, the broad band at *ca.* 3200 cm^{-1} was absent. This confirms the absence of the bands corresponding to the OH3 group, which are not visible in the Raman spectrum, but the vibration of the N–H bond in an NH_4^+ molecule is.

TABLE 6. REFINED SITE SCATTERING (IN ELECTRONS PER SITE, E.P.S.) COMPARED WITH AGGREGATE SITE SCATTERING CALCULATED FROM EMPA ANALYSES FOR THE STUDIED ARROJADITE-(BaNa) CRYSTALS

Site	W1 n.1	W1 n.5
Al	14.6(1)	13.5(1)
Al _{EMPA}	15.63	13.0
M1	21.7(1)	22.5(1)
M2a	26.7(2)	26.1(2)
M2b	23.8(2)	22.7(2)
M3a	20.3(2)	18.9(2)
M3b	20.7(2)	19.6(2)
M4a	23.9(2)	23.5(1)
M4b	23.8(2)	22.6(1)
M5a	26.1(2)	25.7(1)
M5b	25.9(2)	25.8(1)
M6a	25.0(2)	25.0(1)
M6b	25.6(2)	25.6(1)
M7a	24.9(2)	24.2(1)
M7b	25.1(2)	24.9(1)
ΣM	313.4	307.3
ΣM_{EMPA}	312.3	307.3
Ca	19.1(1)	19.9(1)
A1	58.8(2)	58.5(2)
A2	2.0(3)	0.8(1)
B1	12.7(3)	10.2(2)
B2	10.6(3)	10.6(2)
Na1	11.4(2)	11.0(2)
Na2	10.8(3)	10.6(2)
ΣX	125.4	121.6
ΣX_{EMPA}	120.9	120.3

We can conclude that samples from BFR do not contain NH_4^+ , whereas the formula can be calculated considering 3 (OH) groups *apfu*.

DISCUSSION

Arrojadite-(BaNa) from BFR follows the cation-ordering scheme presented by Cámara *et al.* (2006) and Chopin *et al.* (2006) very closely. According to Chopin *et al.* (2006), the ideal structural formula for arrojadite-(BaNa) would be $^{A1}\text{Ba}^{A2}\square^{B1}\text{Na}^{B2}\text{Na}^{Na1,2}\text{Na}_2^{Na3}\square^{Ca}Al^M\text{Fe}_{13}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$. For the arrojadite-(BaNa) samples reported here, there is good agreement between the calculated site scattering values from the chemical formula and the refined site scattering values (Table 6), allowing for a discussion of assignment of cations to crystallographic sites. The data collected from the samples examined in this study were normalized to 12 P and 50 (O + OH + F), following the recommendations in Chopin *et al.* (2006). Using this classification scheme, the dominant

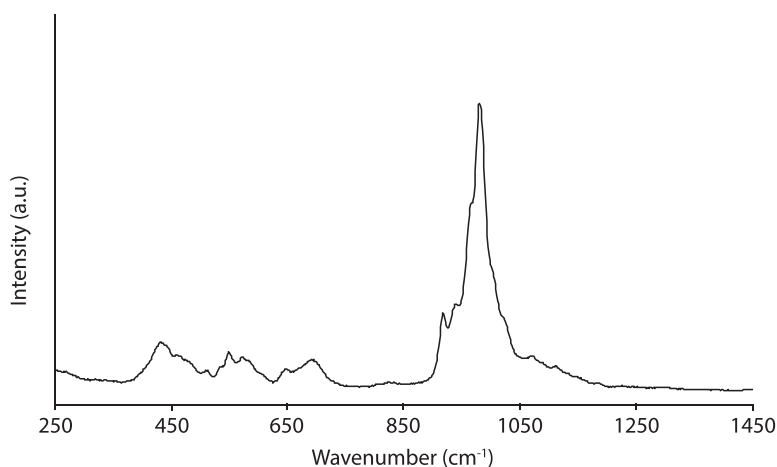


FIG. 4. Fingerprint region of the Raman spectra of arrojadite-(BaNa) from sample W1 n.5.

cation at the $A1 (=X5)$ site is the first suffix, here Ba (1.01 *apfu*). As the Ca site is fully occupied, no other sites are possible locations for the Ba cation. The second suffix was identified as Na by noting that ${}^M\text{Fe}^* = (\text{Fe}^{2+} + \text{Mn}^{2+} + \text{Mg} + \text{Zn}) + \text{Li} - 13 = \Sigma \text{M}^{2+} + \text{Li} - 13$ results in an excess of 0.03 *apfu*, or less than the required 0.5 *apfu* for Fe to be the suffix (Chopin *et al.* 2006). Thus, both $B1 (=X6)$ and $B2 (=X2)$ sites are dominantly occupied by Na. The third possible suffix does not apply to these arrojadite samples from Big Fish River, as $X_T (=2 {}^M\text{Fe}^* + 2 X^{2+} + X^+ - \text{Li} - 1)$ is not

≥ 7.5 and $\Sigma M + \Sigma X$ is not > 20.5 *apfu*, meaning that the $H3x$ site is occupied (no scattering at the $Na3$ site) and no third suffix is used (Chopin *et al.* 2006). Neither $F > 1$ *apfu* nor $\text{Fe}^{3+} > 0.5$ *apfu* occur in these samples and therefore the “fluor” and “ferri” prefixes do not apply.

The M sites are dominated by the divalent cations Fe^{2+} , Mn, and Mg. In W1 n.5, total Al^{3+} is greater than the 1 *apfu* occupancy of the $A1$ site, so the excess Al^{3+} is present at < 0.1 *apfu* at the $M1$ or the $M3a,b$ sites. The $M1$ site is a highly deformed

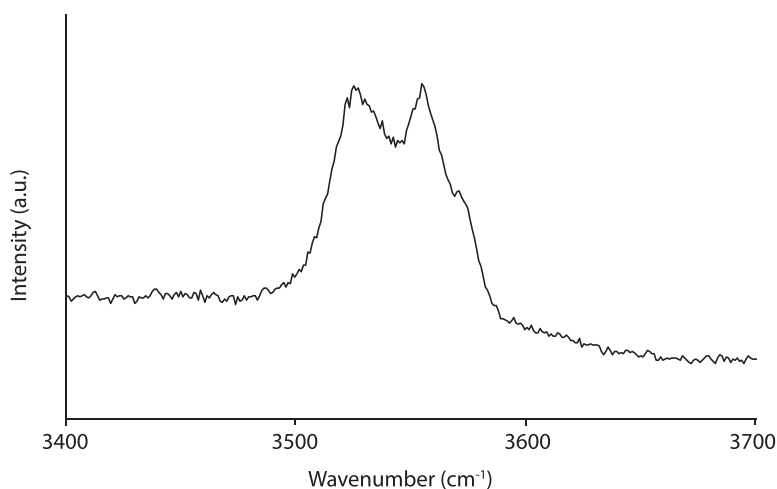


FIG. 5. Raman spectra of the OH-stretching region in arrojadite-(BaNa) from sample W1 n.5. The two clusters of bands with local maxima at 3526 and 3555 cm^{-1} suggest that the non-centrosymmetric space group of Cc is correct for this near-endmember sample.

tetrahedron [bond angle variance of Robinson *et al.* (1971) = 236–243] with a further bond at a long distance of 2.5–2.6 Å. Therefore, two mean bond lengths (m.b.l.) are reported in Table 5. The low site-scattering observed at *M1* sites in all crystals suggests that an element species lighter than Fe is ordered at this site. Magnesium is the best candidate considering the distances in fourfold coordination. In agreement with the other arrojadites studied by Cámara *et al.* (2006), Mg is preferential at the *M3a* and *M3b* sites, followed by the *M4b* and *M2b* sites. Additionally, these data show *M4a* is also preferred to Mg in arrojadite-(BaNa). At the same time, we can observe that Mn^{2+} is preferentially ordered at the *M6* and *M7* sites and in particular at the *M6* and *M7a* sites, which are systematically larger in samples richer in Mn^{2+} ($\langle \text{M6a,b-O} \rangle = 2.196\text{--}2.203$ Å) and consequently also show lower refined site scattering values, but higher than the smaller sites where Mg orders (Table 6). The PO_4 tetrahedra are completely occupied by P in sample W1; no Si was detected in any analyses. Observed m.b.l. (Table 5) are consistent with $\langle \text{P-O} \rangle = 1.531\text{--}1.541$ Å. The *A1* site contains the trivalent cations Al^{3+} and Fe^{3+} , and no other cations (*i.e.*, Sc) were present at this site in this work. Consistently, m.b.l. values range between 1.898 and 1.881 Å (Table 5), while refined site scattering ranges between 13.0(1) and 14.6(1) electrons per site (e.p.s., Table 6), the highest values coincident with the longest m.b.l. The *Ca* site shows preferential occupancy of Ca, with minor Na (≤ 0.05 apfu) and excess Fe^{2+} (0.04–0.12 apfu) [m.b.l. = 2.466–2.478 Å, Table 5; refined site scattering = 19.1(1)–19.9(1) e.p.s., Table 6]. The *Na1* (= *X3*) site is fully occupied by Na cations in both samples [m.b.l. = 2.550–2.575 Å, Table 5; refined site scattering = 11(2)–11.4(2) e.p.s., Table 6]. The *Na2* (= *X2*) site is also dominated by Na cations [m.b.l. = 2.564–2.567 Å, Table 5; refined site scattering = 10.6(1)–10.8(1) e.p.s., Table 6]. While the *B2* site is also occupied by Na cations with minor vacancies [m.b.l. = 2.537–2.547 Å, Table 5; refined site scattering = 10.6(2)–10.6(2) e.p.s., Table 6], the *B1* site shows minor occupancy by Fe^{2+} and Ca (0.03 and 0.02 apfu, respectively) or vacancies [m.b.l. = 2.575 and –2.786 Å, Table 5; refined site scattering = 12.7(1) and 10.2(2) e.p.s., Table 6]. However, the bonding environment of this site is very complex, therefore two m.b.l. have been reported in Table 5, one considering bonds up to 3.3 Å corresponding to vacant sites and another considering fourfold coordination with bond lengths < 2.8 Å, compatible with $^{\text{IV}}\text{Na}$ and with the possible occupation by Fe^{2+} , although the increase of occupancy of Fe at this site drives a shift of the

scattering to slightly different coordinates, as observed by Cámara *et al.* (2006) in arrojadite-(SrFe).

Comparison to arrojadite-(BaNa) from the Luna Albite Pegmatite, Dorio Municipality, Lecco Province, Italy

While arrojadite-(BaNa) from BFR corresponds closely with cation assignments reported by Cámara *et al.* (2006) and Chopin *et al.* (2006) for other arrojadites, there are substantial differences compared to the type specimen described by Vignola *et al.* (2016). Notably, the type specimen has multiple cations occupying the *A1* site (Ba, K, Pb, and Sr) whereas the *A1* site in the BFR specimen is fully occupied by Ba. In addition, the crystal structures from each locality were refined under different parameters. Vignola *et al.* (2016) found that crystal refinement of their data in the *Cc* space group gave a “bad *R1* factor with splitting of several sites and bad anisotropic thermal parameters”. Therefore Vignola *et al.* (2016) chose to refine in the *C2/c* space group starting from the atomic coordinates of arrojadite-(BaFe) in Demartin *et al.* (1996). Using differing space groups resulted in some different, but equivalent, crystallographic sites which can be compared between the samples. At BFR the *A1* (= *X5*) site is completely populated by Ba and minor Na, whereas the type specimen contains mostly Ba, with K, Pb, and Sr (Vignola *et al.* 2016). The *Ca* (= *X1*) site, which generally hosts Ca in arrojadites, including those from BFR, is assigned to Na and instead *M1* is populated by Ca in the type specimen (Vignola *et al.* 2016). In BFR samples, the *M1* site is populated by Fe and Mg and the *Ca* (= *X1*) site contains Ca in all crystal fragments. This assignment of Ca to the *M* sites and, more important, the substitution of Ca by Na at the *Ca* sites, was not foreseen in the arrojadite-group classification. Therefore, this poses a problem in the classification of the sample from the Luna albite pegmatite. In particular, dominance of Na at the *Ca* site (= *X1*) would change the charge arrangements schemes discussed by Chopin *et al.* (2006) and, along with the ordering of Ca at the *M1* site, needs crystal chemical support. This support is not evident from the data in Vignola *et al.* (2016), which show up to four distances < 2.07 Å (one is even < 1.95 Å). Despite these differences, the unit cell reported for arrojadite-(BaNa) from BFR closely corresponds to the type specimen (Table 7). A comparison with other arrojadite-group minerals, along with other physical properties, is reported in Table 7.

Electron microprobe results indicate that arrojadite sample W1 from BFR is the closest known specimen

to endmember arrojadite-(BaNa), with 1.01 *apfu* Ba at the *A1* (= *X5*) site and 0.90–0.96 *apfu* Na at the *B1* site. In the type specimen from the Luna albite pegmatite the *A1* (= *X5*) site is shared with 0.62 *apfu* Ba as the dominant cation, 0.27 *apfu* K, 0.13 *apfu* Pb, and 0.07 *apfu* Sr (Vignola *et al.* 2016). Furthermore, the Luna albite pegmatite sample contains 0.25 *apfu* F, whereas arrojadite-(BaNa) from BFR has no F measurable above the 500 ppm detection limit, similar to the low F (0.02 wt.%) measured in arrojadite-(KNa), also from the Rapid Creek Formation (Cámara *et al.* 2006).

As expected, the Raman spectra of arrojadite-(BaNa) show many similarities between the relative locations of the phosphate modes between the two localities. However, the presence of two clusters of bands, with local maxima at 3526 and 3555 cm^{-1} , suggests a non-centrosymmetric *Cc* space group is correct for the Big Fish River sample. If the actual space group was *C2/c*, these two clusters of bands would be expected to merge. It is noteworthy that in the type specimen only one peak at 3522 cm^{-1} was observed (Vignola *et al.* 2016), supporting the centrosymmetric *C2/c* space group for arrojadite-(BaNa) from the Luna albite pegmatite.

Differences in the crystallographic structure and chemistry between these two samples of arrojadite-(BaNa) may be attributed to the different genetic environments and thermodynamic conditions in which they formed. The sedimentary Rapid Creek Formation which hosts arrojadite-(BaNa) in veins, phosphatic nodules, and shale beds at Big Fish River is a phosphatic siderite-rich ironstone (Young & Robertson 1984). Arrojadite-group minerals precipitated early in the paragenetic sequence from low-salinity fluids in secondary hydrothermal veins in open fractures during or after the Laramide orogeny, under very low-grade metamorphic conditions with a minimum temperature of 180–200 °C at unknown pressure (Robinson *et al.* 1992). These minerals formed as part of a Fe-Mg-rich association, where the surrounding siderite-rich host rock provided a consistent supply of Fe, Mn, and Mg to P-rich, Na-bearing fluids throughout the entire period of crystallization (Robertson 1982, Robinson *et al.* 1992). The low crystallization temperature led to an ordering of the structure, making evident the absence of the center of symmetry, resulting in well ordered arrojadite-(BaNa) crystallized in the non-centrosymmetric *Cc* space group.

Arrojadite-(BaNa) from the Luna albite pegmatite formed in an igneous environment under significantly higher temperature and pressure conditions than the samples studied here. The Luna albite pegmatite is a member of the Piona pegmatite swarm in northern Italy, which intruded into high-grade metapelites

between 229 ± 7 Ma and 208 ± 4 Ma (Sanders *et al.* 1996). Sanders *et al.* (1996) proposed an anatectic origin for these pegmatites through the melting of a pelitic protolith. The Piona pegmatite swarm had a crystallization temperature of 550 ± 50 °C and was emplaced under pressures of up to 3.5–5 kbar (Sanders *et al.* 1996). Arrojadite-(BaNa) occurs in the blocky-plagioclase zone as masses or roughly crystallized individuals as a primary magmatic phosphate mineral associated with albite and fluorapatite (Vignola *et al.* 2016). Primary Fe-Mn phosphates, including graftonite, sarcopside, and triphylite, also occur in the Luna pegmatite with quartz, albite/oligoclase, muscovite, and minor almandine-rich garnet and schorl (Vignola *et al.* 2011). In the Luna albite pegmatite, crystallization occurred under higher temperatures and pressures of formation than the phosphates at BFR, resulting in increased disorder and thus a better agreement with a model for arrojadite-(BaNa) in the centrosymmetric *C2/c* space group as described by Vignola *et al.* (2016).

CONCLUSIONS

Near-endmember arrojadite-(BaNa) has been discovered in the phosphatic ironstones of Big Fish River, Yukon, Canada. Crystallographic and chemical analyses show significant differences between the type specimen from Luna albite pegmatite, Dorio municipality, Lecco Province, Italy (Vignola *et al.* 2016) and this occurrence. Chemical analyses of arrojadite-(BaNa) from Luna albite pegmatite show the *A1* (= *X5*) site to contain 0.62 *apfu* Ba in addition to minor K, Pb, and Sr (Vignola *et al.* 2016), which is substantially less than the 1.01 *apfu* Ba in sample W1 from BFR. Furthermore, BFR specimens contain no measurable F, whereas 0.25 *apfu* F is reported by Vignola *et al.* (2016). In addition to chemistry, crystal structure refinement was completed in the *Cc* space group in this study, whereas the *C2/c* space group was used by Vignola *et al.* (2016). The variance may be explained as a result of the differing temperature and pressure conditions of the environments in which the samples crystallized. Arrojadite-(BaNa) from the Luna albite pegmatite crystallized under high temperature and pressure conditions, resulting in a disordered structure with diffraction data giving a better fit using a centrosymmetric model, whereas arrojadite-(BaNa) from BFR formed in a low temperature setting, resulting in a decrease in symmetry and more order, thus obtaining a better agreement with a non-centrosymmetric structure model. Major differences in site assignment include the *Ca* (= *X1*) site hosting Na in the type specimen and Ca in BFR

TABLE 7. COMPARISON OF THE PHYSICAL PROPERTIES FOR SELECTED MINERALS OF THE ARROJADITE SUBGROUP

Mineral Locality Reference	Arrojadite-BaNa Big Fish River, Canada This work	Arrojadite-(BaNa) Luna pegmatite, Italy Vignola <i>et al.</i> (2016)	Arrojadite-(BaFe) Alpe Groppera, Italy [1, 2, 3]
Ideal formula	$\text{BaNa}_3(\text{NaCa})\text{Fe}^{2+}_{13}\text{Al}$ (PO_4) ₁₁ (PO_3OH) OH_2	$\text{BaNa}_3(\text{NaCa})\text{Fe}^{2+}_{13}\text{Al}$ (PO_4) ₁₁ (PO_3OH) OH_2	$\text{BaNa}_3(\text{CaFe})\text{Fe}^{2+}_{13}\text{Al}$ (PO_4) ₁₂ OH_2
Space group	<i>Cc</i>	<i>C2/c</i>	<i>C2/c</i> or <i>Cc</i>
<i>a</i> (Å)	16.5163 (8)	16.4984(6)	16.406(5)
<i>b</i> (Å)	10.0067 (5)	10.0228(3)	9.945(3)
<i>c</i> (Å)	24.5435 (12)	24.648(1)	24.470(5)
β (Å)	106.121 (2)	105.850(4)	105.73(2)
<i>V</i> (Å ³)	3896.9 (3)	3920.8(2)	3843(2)
<i>Z</i>	4	4	4
Strongest	—	—	—
X-ray lines	—	—	—
	4.637(18)	4.621(22)	4.56(27)
	—	3.488(28)	3.4(31)
	3.390(17)	3.400(16)	3.310(20)
	3.202(47)	3.303(46)	3.211(47)
	3.040(100)	3.137(100)	3.032(100)
	—	2.954(21)	2.841(34)
	2.834(24)	2.936(22)	2.828(30)
	—	2.910(15)	2.824(27)
	—	—	—
	—	2.878(32)	2.797(16)
	—	—	—
	—	—	—
	2.757(27)	2.861(20)	2.758(32)
	2.699(30)	—	—
	2.545(35)	2.818(61)	2.706(39)
	2.195(19)	—	2.703(68)
	1.910(18)	2.667(35)	2.543(38)
Density	3.62	3.535(1)	3.54
Hardness	—	4–5	—
Color	Colorless to grey, transparent	Pale grayish-green, translucent	Grayish-green, translucent
Morphology	Tabular platy crystals	Aggregates of numerous grains	Aggregates of numerous grains

Augmented and modified from Vignola *et al.* (2016). [1] Demartin *et al.* (1996), [2] Cámara *et al.* (2006), [3] Chopin *et al.* (2006).

samples, and the *M1* site being populated by Ca in the sample from the Luna albite pegmatite compared to Fe and Mg in this study. Raman data collected in this study show the presence of two clusters of bands in the 3500–3600 cm⁻¹ range that support that the appropriate space group for arrojadite-(BaNa) from Big Fish River is *Cc*, which differs from the *C2/c* space group of the centrosymmetric arrojadite-(BaNa) from the Dorio municipality (Vignola *et al.* 2016). As of yet, the sample W1 n.5 from this study is the closest to the endmember composition of arrojadite-(BaNa).

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TABLE 7. CONTINUED.

Arrojadite-(PbFe) Sapuçaica, Brazil [2, 3]	Arrojadite-(SrFe) Horrjoberg, Sweden [2, 3]	Arrojadite-(KNa) Rapid Creek, Canada [2, 3]
$\text{PbFe}^{2+}(\text{Ca},\text{Na})_2\text{Fe}^{2+}_{13}\text{Al}$ $(\text{PO}_4)_{11}(\text{PO}_3\text{OH})\text{OH}_2$ <i>Cc</i>	$\text{SrFe}^{2+}(\text{Ca},\text{Na})_2\text{Fe}^{2+}_{13}\text{Al}$ $(\text{PO}_4)_{11}(\text{PO}_3\text{OH})\text{OH}_2$ <i>Cc</i>	$\text{KNa}_3(\text{Ca},\text{Na})_2\text{Fe}^{2+}_{13}\text{Al}$ $(\text{PO}_4)_{11}(\text{PO}_3\text{OH})\text{OH}_2$ <i>Cc</i>
16.4304(9)	16.3992(7)	16.5220(11)
9.9745(5)	9.9400(4)	10.0529(7)
24.5869(13)	24.4434(11)	24.6477(16)
105.485(2)	105.489(1)	106.509(2)
3883.2(5)	3839.76(46)	3932.2(7)
4	4	4
—	—	5.861(29)
—	—	5.026(27)
4.553(25)	—	—
3.396(24)	3.378(26)	—
3.305(22)	3.293(21)	—
3.208(43)	3.192(41)	3.186(33)
3.019(100)	3.009(100)	3.050(100)
—	—	2.853(22)
2.829(35)	2.82(23)	—
2.819(33)	—	—
2.813(29)	—	—
—	2.805(28)	2.798(25)
—	—	2.793(28)
—	—	2.777(24)
2.750(29)	—	2.753(23)
—	2.737(28)	—
2.694(32)	2.685(70)	2.691(71)
2.690(55)	—	—
2.538(30)	2.529(23)	—
3.65	3.57	3.44
4–5	—	—
Pale honey, transparent	—	Yellow, transparent
Granular masses or subhedral crystals	—	Stout platy prismatic crystals

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REFERENCES

- BRUKER (2003) SMART (Version 5.634) and SAINT (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, United States.
- CÁMARA, F., OBERTI, R., CHOPIN, C., & MEDENBACH, O. (2006) The arrojadite enigma: I. A new formula and a new model for the arrojadite structure. *American Mineralogist* **91**, 1249–1259.
- CÁMARA, F., BITTARELLO, E., CIRIOTTI, M.E., NESTOLA, F., RADICA, F., & BRACCO, R. (2015) Fluorcarmoite-(BaNa), IMA 2015-062. CNMNC Newsletter No. 27, October 2015. *Mineralogical Magazine* **79**, 1229–1236.
- CHOPIN, C., OBERTI, R., & CÁMARA, F. (2006) The arrojadite enigma: II. Compositional space, new members and nomenclature of the group. *American Mineralogist* **91**, 1260–1270.
- COLEMAN, L.C. & ROBERTSON, B.T. (1981) Nahpoite Na_2HPO_4 , a new mineral from the Big Fish River area, Yukon Territory. *Canadian Mineralogist* **19**, 373–376.
- DELLA VENTURA, G., BELLATRECCIA, F., RADICA, F., CHOPIN, C., & OBERTI, R. (2014) The arrojadite enigma III. The incorporation of volatiles: A polarised FTIR spectroscopy study. *European Journal of Mineralogy* **26**, 679–688.
- DEMARTIN, F., GRAMACCIOLI, C.M., PILATI, T., & SCIESA, E. (1996) Sigismundite, $(\text{Ba},\text{K},\text{Pb})\text{Na}_3(\text{Ca},\text{Sr})(\text{Fe},\text{Mg},\text{Mn})_{14}(\text{OH})_2(\text{PO}_4)_{12}$, a new Ba-rich member of the arrojadite group from Spluga valley, Italy. *Canadian Mineralogist* **34**, 827–834.

- FROST, R.L., XI, Y., SCHOLZ, R., & CAMPOS HORTA, L.F. (2013) The phosphate mineral arrojadite-(KFe) and its spectroscopic characterization. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **109**, 138–145.
- HEADEN, W.P. (1891) A new phosphate from the Black Hills of South Dakota. *American Journal of Science* **41**, 415–417.
- HEINRICH, K.F.J. (1987) Mass absorption coefficients for electron probe microanalysis. In *Proceedings of the 11th International Congress on X-Ray Optics and Microanalysis* (J. Brown & R. Packwood, eds.). University of Western Ontario, London, Ontario, Canada (67–119).
- MANDARINO, J.A., STURMAN, B.D., & CORLETT, M.I. (1978) Satterlyite, a new hydroxyl-bearing ferrous phosphate from the Big Fish River area, Yukon Territory. *Canadian Mineralogist* **16**, 411–413.
- MOMMA, K. & IZUMI, F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **44**, 1272–1276.
- MOORE, P.B., ARAKI, T., MERLINO, S., MELLINI, M., & ZANAZZI, P.F. (1981) The arrojadite-dickinsonite series. $\text{KNa}_4\text{Ca}(\text{Fe,Mn})^{2+}_{14}\text{Al}(\text{OH})_2(\text{PO}_4)_{12}$: Crystal structure and crystal chemistry. *American Mineralogist* **66**, 1034–1049.
- POUCHOU, J.-L. & PICOIR, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model “PAP”. In *Electron Probe Quantitation* (K.F.J. Heinrich & D.E. Newbury, eds.). Plenum Publishing Corporation, New York City, New York, United States (31–75).
- REED, S.J.B. (1990) Fluorescence effects in quantitative microprobe analysis. In *Microbeam Analysis – 1990* (D.B. Williams, P. Ingram, & J.R. Michael, eds.). San Francisco Press, San Francisco, California, United States (109–114).
- ROBERTSON, B.T. (1982) Occurrence of epigenetic phosphate minerals in a phosphatic iron-formation, Yukon Territory. *Canadian Mineralogist* **20**, 177–187.
- ROBINSON, K., GIBBS, G.V., & RIBBE, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science* **172**, 567–570.
- ROBINSON, G.Q., VAN VELTHUIZEN, J., ANSELL, H.G., & STURMAN, B.D. (1992) Mineralogy of the Rapid Creek and Big Fish River area, Yukon Territory. *Mineralogical Record* **23**, 1–47.
- SANDERS, C.A., BERTOTTI, G., TOMMASINI, S., DAVIES, G.R., & WIJBRANS, J.R. (1996) Triassic pegmatites in the Mesozoic middle crust of the Southern Alps (Italy): Fluid inclusions, radiometric dating and tectonic implications. *Eclogae Geologicae Elvetiae* **89**, 505–525.
- SHELDRIK, G.M. (2015) Crystal structure refinement with SHELXL. *Acta Crystallographica* **C71**, 3–8.
- SPRINGER, G. (1971) *Fluorescence by the X-ray continuum in multi-element targets*. Falconbridge Nickel Mines Limited, Thornhill, Ontario, Canada. Report FRL-138, 14 pp.
- ŠTEVKO, M., SEJKORA, J., UHER, P., CÁMARA, F., ŠKODA, R., & VACULOVÍČ, T. (2018) Fluorarrojadite-(BaNa), $\text{BaNa}_4\text{CaFe}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})\text{F}_2$, a new member of the arrojadite group from Gemerská Poloma, Slovakia. *Mineralogical Magazine* **82(4)**, 863–876.
- STURMAN, B.D. & MANDARINO, J.A. (1976) Baričite, the magnesium analogue of vivianite from Yukon Territory, Canada. *Canadian Mineralogist* **14**, 403–406.
- STURMAN, B.D., MANDARINO, J.A., & CORLETT, M.J. (1977) Maričite, a sodium iron phosphate, from the Big Fish River area, Yukon Territory, Canada. *Canadian Mineralogist* **15**, 396–398.
- STURMAN, B.D., MANDARINO, J.A., MROSE, M.E., & DUNN, P.J. (1981a) Gormanite, $\text{Fe}_2^{2+}\text{Al}_4(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, the ferrous analogue of souzalite, and new data for souzalite. *Canadian Mineralogist* **19**, 381–387.
- STURMAN, B.D., PEACOR, D.R., & DUNN, P.J. (1981b) Wicksite, a new mineral from northeastern Yukon Territory. *Canadian Mineralogist* **19**, 377–380.
- TOBY, B.H. & VON DREELE, R.B. (2013) GSAS-II: the genesis of a modern open-source all-purpose crystallography software package. *Journal of Applied Crystallography* **46(2)**, 544–549.
- VIGNOLA, P., DIELLA, V., FERRARI, E.S., & FRANSOLET, A.-M. (2011) Complex Mechanisms of Alteration in a gaffonite + sarcopside + triphylite association from the Luna Pegmatite, Piona, Lecco Province, Italy. *Canadian Mineralogist* **49**, 765–776.
- VIGNOLA, P., HATERT, F., BAIJOT, M., DAL BO, F., ANDÒ, S., BERSANI, D., PAVESE, A., RISPLENDETE, A., & VANINI, F. (2016) Arrojadite-(BaNa), $\text{BaNa}_3(\text{Na,Ca})\text{Fe}^{2+}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$, a new phosphate mineral from the Luna albite pegmatite, Dorio commune, Lecco province, Italy. *Canadian Mineralogist* **54**, 1021–1032.
- WILLIAMS, K.L. (1987) *Introduction to X-ray Spectrometry: X-ray Fluorescence and electron microprobe analysis*. Allen and Unwin, London, England, 370 pp.
- WILSON, A.J.C. (1992) *International Tables for X-ray Crystallography, Vol. C*. Kluwer Academic Press, London, England.
- YOUNG, F.G. & ROBERTSON, B.T. (1984) The Rapid Creek Formation: An Albian flysch-related phosphatic iron formation in northern Yukon Territory. *Canadian Society of Petroleum Geologists Special Publications - Memoir* **9**, 361–372.

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