Fluorarrojadite-(BaNa), $BaNa_4CaFe_{13}Al(PO_4)_{11}(PO_3OH)F_2$, a new member of the arrojadite group from Gemerská Poloma, Slovakia

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Abstract: The new mineral fluorarrojadite-(BaNa), ideally $BaNa_4CaFe_{13}Al(PO_4)_{11}(PO_3OH)F_2$ was found on the dump of of Elisabeth adit near Gemerská Poloma, Slovakia. It occurs in hydrothermal quartz veins intersecting highly fractionated, topaz-zinnwaldite S-type leucogranite. Fluorarrojadite-(BaNa) is associated with fluorapatite, "fluordickinsonite-(BaNa)", triplite, viitaniemiite and minor amounts of other minerals. It forms fine grained

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irregular aggregates up to 4 x 2 cm, which consists of individual anhedral grains up to 0.01 mm in size. It has a yellowish-brown to greenish-yellow colour, very pale yellow streak, a vitreous to greasy lustre. Mohs hardness is about 4½ to 5. The fracture is irregular and the tenacity is brittle. The measured density is 3.61(2) $g \cdot cm^{-3}$ and calculated density is 3.650 $g \cdot cm^{-3}$. Fluorarrojadite-(BaNa) is biaxial (+) and nonpleochroic. The calculated refractive index based on empirical formula is 1.674. The empirical formula (based on 47 O and 3 (OH+F) *apfu*) is

$^{A1}(Ba_{0.65}K_{0.35})_{\Sigma 1.00}{}^{A2}Na_{0.35}{}^{B1}(Na_{0.54}Fe_{0.46})_{\Sigma 1.00}{}^{B2}Na_{0.54}{}^{Ca}(Ca_{0.74}Sr_{0.20}Pb_{0.02}Ba_{0.04})_{\Sigma 1.00}Na_2{}^{Na3}Na_{0.46}$ $^{M}(Fe_{7.16}Mn_{5.17}Li_{0.37}Mg_{0.12}Sc_{0.08}Zn_{0.06}Ga_{0.02}Ti_{0.02})_{\Sigma 13.00}Al_{1.02}P_{11}O_{44}PO_{3.56}(OH)_{0.54}{}^{W}(F_{1.54}OH_{0.46})$. Fluorarrojadite-(BaNa) is monoclinic, space group *Cc*, a = 16.5563(6) Å, b = 10.0476(6) Å, c = 24.669(1) Å, β = 105.452(4)°, V = 3957.5(4) Å^3 and Z = 4. The seven strongest reflections in the powder X-ray diffraction pattern are [d_{obs} in Å, (I), *hkl*: 3.412, (21), 116; 3.224, (37), 206; 3.040, (100), 42-4; 2.8499, (22), 33-2; 2.7135, (56), 226; 2.5563, (33), 028 and 424; 2.5117, (23), 040. The new mineral is named according to the actual nomenclature scheme of arrojadite group minerals, which was approved by the CNMNC IMA. In fluorarrojadite-(BaNa) Fe^{2+} is a dominant cation at the M site (so the root-name is arrojadite) and two suffixes are added to the root-name according to the dominant cation of the dominant valence state at the A1 (Ba^{2+}) and B1 sites (Na^{+}). A prefix fluor is added to the root-name as F^{-} is dominant over (OH^{-}) at the W site.

Key-words: fluorarrojadite-(BaNa); new mineral; arrojadite group; phosphates; Raman spectroscopy; S-type granite; Gemerská Poloma; Slovakia

Running title: Fluoarrojadite-(BaNa), a new member of arrojadite group

Introduction

Fluorarrojadite-(BaNa), ideally $BaNa_4CaFe_{13}Al(PO_4)_{11}(PO_3OH)F_2$ is a new member of arrojadite group. It was found at the dump of Elisabeth adit near Gemerská Poloma village, Rožňava Co., Košice Region, Slovak Republic.

The new mineral is named according to actual nomenclature scheme of arrojadite group minerals (Chopin *et al.*, 2006), which was approved by the CNMNC IMA and it is based on the occupancy of M (root-name), A1 (first suffix), B1 (second suffix) and W (first prefix) sites. Three root-names are recognized for arrojadite group minerals: arrojadite (Fe^{2+} dominant at M sites), dickinsonite (Mn^{2+} dominant at M sites) and carbonoite (Mg dominant at the M sites; successively found and approved by the CNMNC IMA, Cámara *et al.*, 2015). General structural formula for arrojadite group minerals is $A_2B_2CaNa_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$ (for details see Chopin *et al.,* 2006). In fluorarrojadite-(BaNa) Fe^{2+} is dominant cation at the M site (so the root-name is arrojadite) and two suffixes are added to the root-name according to the dominant cation of the dominant valence state at the A1 (Ba^{2+}) and B1 sites (Na^{+}). Prefix fluor is added to the root-name as F^{-} is dominant over $(OH)^{-}$ at the W site.

The new mineral and the name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2016-075). The description of fluorarrojadite-(BaNa) is based upon two holotype specimens (two parts of one large piece). One is deposited in the collections of the Department of Mineralogy and Petrology, National Museum in Prague, Cirkusová 1740, 19300 Praha 9, Czech Republic under the catalogue number P1P 13/2016. The second holotype specimen is deposited in the collections of the Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 84215 Bratislava IV, Slovak Republic under the catalogue number 7401.

Occurrence

Several specimens with fluorarrojadite-(BaNa) were found at the dumps of Elisabeth adit (which exploited Gemerská Poloma talc deposit) situated near Gemerská Poloma village, Rožňava Co., Košice Region, Slovak Republic (48°45'04.06" N, 20°29'39.27" E). During the exploration of the talc-magnesite deposit main crosscut of Elisabeth adit intersected large body of specialized S-type granite (also called Gemeric granite) with the abundant hydrothermal quartz veins containing fluorarrojadite-(BaNa).

The granitic rocks of the Gemeric Unit represent a distinct type of specialized (Sn-W-F), highly evolved suite with S-type affinity, which differs from other granitoids occurring in the Veporic and Tatric Units of the Western Carpathian crystalline basement; they are enriched in phosphorus and rare lithophile elements, such as Li, Rb, Cs, B, Ga, Sn, W, Nb, Ta, U and depleted in REE, Zr, Ti, Sr, Ba (e.g., Uher and Broska, 1996; Petrík and Kohút, 1997; Kubiš and Broska, 2005; Kubiš and Broska, 2010; Breiter *et al.,* 2015). The Gemeric granitic rocks forms several small plutons intruded to the intensively folded Lower Paleozoic (mainly Ordovician to Devonian) volcano-sedimentary complex of the Gelnica Group, metamorphosed in the greenschist metamorphic facies (Bajaník *et al.,* 1984; Petrasová *et al.,* 2007). In the Gemerská Poloma area, the metamorphic rocks are composed mainly of phyllites, metaporphyroclastic rocks of rhyolitic to dacitic composition, locally with lenses of metadolomite and strongly steatitized magnesite with recently exploited talc deposit near Gemerská Poloma (Kilík, 1997). The age of granite intrusion and related hydrothermal veins with fluorarrojadite-(BaNa) and other phosphates is Late Permian (~260 to 250 Ma), on the basis of zircon U-Pb dating of the granites (Poller *et al.,* 2002) and Re-Os molybdenite dating of related Sn-W-Mo mineralization (Kohút and Stein, 2005).

Several types of the Gemeric granites were distinguished at the Gemerská Poloma area: (**a**) coarse-grained porphyritic granite to granite porphyry, (**b**) medium-grained Li-

annite-topaz-tourmaline bearing granite, (**c**) P-enriched topaz-zinnwaldite leucogranite and (**d**) albitite (Dianiška *et al.,* 2002; Dianiška *et al.,* 2007; Petrík *et al.,* 2014; Breiter *et al.,* 2015). Except of albitites, all listed types of granite were recently encountered in the Elisabeth adit (Števko *et al.,* 2015).

The hydrothermal quartz veins with albite, muscovite, fluorite, siderite, calcite, dolomite, sulphides and sulphosalts were observed in all types of granite, but the occurrence of the quartz veins with fluorarrojadite-(BaNa) and other phosphates (fluorapatite,"fluordickinsonite-(BaNa)", triplite and viitaniemiite) is limited only to the highly fractionated topaz-zinnwaldite leucogranite (Števko *et al.,* 2015). The quartz veins with fluorarrojadite-(BaNa) are up to 8 cm thick and no more than 20 cm long and except of other phosphates (common and macroscopic: fluorapatite and triplite; rare and microscopic: viitaniemiite; very rare and microscopic: "fluordickinsonite-(BaNa)") they contain minor amounts of albite, orthoclase, muscovite, fluorite, Mn-rich siderite to rhodochrosite, arsenopyrite, pyrite, bismuthinite, kobellite, tintinaite, giessenite and native bismuth.

Physical and optical properties

Fluorarrojadite-(BaNa) occurs as very fine grained irregular aggregates usually up to 1 x 1 cm in size, exceptionally up to 4 x 2 cm (Figure 1), which consists of individual anhedral grains up to 0.01 mm. Individual crystals have not been observed. It has a yellowish-brown to greenish-yellow colour, very pale yellow streak, a vitreous to greasy lustre and is non-fluorescent in SW and LW ultraviolet light. The Mohs hardness is estimated at about 4½ to 5 based upon scratch tests and by analogy to other arrojadite group minerals. The fracture is irregular and tenacity is brittle. No cleavage was observed as aggregates of fluorarrojadite-(BaNa) are fine grained. The measured density acquired by floating of the mineral fragments in a mixture of the Clerici solution (density 4.2 g·cm^{-3}) and distilled water is 3.61(2) g·cm^{-3}, whereas calculated density is 3.650 g·cm^{-3} based on the empirical formula and unit-cell

123 volume. Fluorarrojadite-(BaNa) is opticaly biaxial (+) without apparent pleochroism.
124 Refractive indexes and other optical properties were not determined due to very small single
125 grain size. The calculated refractive index based on the empirical formula is 1.674.
126
127 **Raman spectroscopy**
128 Raman spectrum of fluorarrojadite-(BaNa) was collected in the range 3580-50 cm^{-1}
129 using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on confocal
130 Olympus microscope at the Department of Mineralogy and Petrology, National Museum,
131 Prague, Czech Republic. The Raman signal was excited by a green 532 nm diode-pumped
132 solid-state laser and detected by a CCD detector. The experimental parameters were: 10x
133 objective, 1 s exposure time, 1000 exposures, 900 lines/mm grating, 50 µm slit spectrograph
134 aperture and 8 mW laser power level. The instrument was set up by a software-controlled
135 calibration procedure using multiple neon emission lines (wavelength calibration), multiple
136 polystyrene Raman bands (laser frequency calibration) and standardized white-light sources
137 (intensity calibration). Spectral manipulations were performed using the Omnic 9 software
138 (Thermo Scientific).
139 Raman spectrum (Figure 2a-c) of fluorarrojadite-(BaNa) is similar to spectra published
140 by Frost *et al.* (2013) for arrojadite-(KFe) as same as to those from RRUFF database
141 (www.rruff.info, Lafuente *et al.* 2015) - arrojadite-(KNa) (R050107), arrojadite-(KFe)
142 (R070316) and arrojadite-(NaFe) (R-070298). The existence of several non-equivalent $(PO_4)^{3-}$
143 groups, their strong distortion and presence of $(PO_3OH)^{2-}$ group in the crystal structure of
144 proposed new mineral lead to complex Raman spectrum with a lot of overlapping bands
145 corresponding to stretching and bending vibrations of phosphate groups (Nakamoto, 1986).
146 The most intensive bands in the region 1060 - 830 cm^{-1} (1020, 985, 959, 939, 916 and 839
147 cm^{-1}) corresponds to ν_1 symmetric stretching vibration of $(PO_4)^{3-}$ and $(PO_3OH)^{2-}$ groups; those

148 at 1151, 1113 and 1076 cm^{-1} to ν_3 antisymmetric stretching vibration of $(PO_4)^{3-}$ and
149 $(PO_3OH)^{2-}$ groups. The bending vibrations of $(PO_4)^{3-}$ and $(PO_3OH)^{2-}$ groups are represented
150 by bands in the region with frequencies between 700 and 400 cm^{-1}: 507, 481, 461, 439 and
151 414 cm^{-1} (ν_2) and 643, 602, 580, 575, 551 and 532 cm^{-1} (ν_4). The observed bands at 3551 and
152 3523 cm^{-1} are connected to stretching vibrations of OH groups. These compare well with
153 stretching vibrations observed by Cámara *et al.* (2006) in Nickel Plate mine arrojadite-(KFe)
154 and Rapid Creek arrojadite-(KNa) and also with FTIR absorbance data by Della Ventura *et al.*
155 (2014) for Nickel Plate mine arrojadite-(KFe). Note, the absence of molecular water in the
156 studied mineral phase is confirmed by no observed bands in the area 1650 – 1550 cm^{-1}.

157 **Chemical composition**

158 Quantitative chemical analyses (5 points) of fluorarrojadite-(BaNa) were performed at
159 the Laboratory of Electron Microscopy and Microanalysis of the Masaryk University and
160 Czech Geological Survey in Brno, Czech Republic on the Cameca SX100 electron
161 microprobe equipped with five wavelength-dispersive spectrometers. Analytical conditions
162 were following: 15 kV accelerating voltage, 10 nA beam current, 10 μm beam diameter and
163 WDS mode. Raw X-ray intensities were corrected for matrix effects with a φ(ρz) algorithm
164 (Pouchou and Pichoir, 1991).

165 The contents of trace elements in fluorarrojadite-(BaNa) were determined by LA-ICP-
166 MS at Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech
167 Republic. The setup consists of laser ablation system UP213 (New Wave, USA) and
168 quadrupole ICP-MS Agilent 7500ce (Agilent Technologies, Japan). Ablation system is
169 equipped with Nd:YAG laser emitting radiation with wavelength of 213 nm. Laser ablation
170 was performed with a single hole drilling mode for the duration of 60 seconds for each spot of
171 100 μm diameter, laser fluency of 12 J cm^{-2}, and repetition rate of 10 Hz. The LA-ICP-MS
172 measurements were normalized on average electron-microprobe measured concentration of

phosphorus in fluorarrojadite-(BaNa) and the NIST SRM 610 glass reference material was used. Analytical data for fluorarrojadite-(BaNa) as well as standards used are given in Table 1 and the LA-ICP-MS analyses of selected trace elements in fluorarrojadite-(BaNa) are given in Table 2.

The average composition of fluorarrojadite-(BaNa) corresponds to the empirical formula (based on 47 O OH + F = 2 + [21 – the sum of non-(P,Al) cations] *apfu*, Chopin *et al.* 2006):

$(Na_{3.96}Ca_{0.74}Ba_{0.69}K_{0.35}Sr_{0.20}Pb_{0.02})_{\Sigma 5.96}{}^{M}(Fe_{7.62}Mn_{5.17}Li_{0.37}Mg_{0.12}Sc_{0.08}Zn_{0.06}Ti_{0.02}Ga_{0.02})_{\Sigma 13.46}Al_{1.02}(P_{12.02}O_{47})(F_{1.54}OH_{1.00}O_{0.46})_{\Sigma 3.00}$. The elements have been grouped into four categories: large low- charge cations (alkali and alkaline earth metals plus lead occupying high coordination number sites; small alkali and alkaline earth metals plus transition metals in four-, five- and six-fold coordinated sites; Al (Ga) in small octahedra and P in tetrahedral coordination. The sum of [Fe+Mn+Mg+Li+(Sc,Zn,Ti)] > 13 *apfu*, but it is < 13.5 therefore precluding dominance of Fe (or Mn) in the B1 type sites described by Chopin *et al.* (2006). In addition, the sum of alkali and alkaline earths metals close to 6 *apfu*, out of them 1.69 are divalent cations (essentially Ca and Ba), and this implies that the formula scheme has to be no. 3 in Table 3 of Chopin *et al.* (2006). Therefore, Ba must be dominant at A1 site and Na at B1 site. Furthermore, the analysed fluorine content is F > 1.5 *apfu*, distinguishing it from the composition reported by Vignola *et al.* (2015), and thus this mineral has to be classified as fluorarrojadite-(BaNa).

In absence of site partitioning that can be obtained only from crystal structure refinement (see below), site assignment follows the cation ordering scheme proposed by Cámara *et al.* (2006), allow to guess the ordering of the cations in the different sites of the structure, thus leading to the following crystal-chemical formula:

$^{A1}(Ba_{0.65}K_{0.35})_{\Sigma 1.00}{}^{A2}Na_{0.35}{}^{B1}(Na_{0.54}Fe_{0.46})_{\Sigma 1.00}{}^{B2}Na_{0.54}{}^{Ca}(Ca_{0.74}Sr_{0.20}Pb_{0.02}Ba_{0.04})_{\Sigma 1.00}Na_2{}^{Na3}Na_{0.46}$

$^{M}(Fe_{7.16}Mn_{5.17}Li_{0.37}Mg_{0.12}Sc_{0.08}Zn_{0.06}Ga_{0.02}Ti_{0.02})_{\Sigma 13.00}Al_{1.02}P_{11}O_{44}PO_{3.46}(OH)_{0.54}{}^{W}(F_{1.54}OH_{0.46})_{\Sigma 2.00}$. The presence of 0.46 *apfu* of Fe^{2+} at B1 sites implies that B2 can be at most occupied by 0.56 *apfu* of Na, the remaining Na occupying partially the Na3 site. This implies that in the calculation of total amount of (F+OH), the Na present at Na3 site must be subtracted to 3 (F+OH), because the occupancy of the Na3 site is incompatible with a proton bonded to the O3x anion site at the PO_4 group at P1x site (see Cámara *et al*. 2006 for a discussion of local ordering). Although Raman spectrum does not show a clear indication of a deprotonation of the PO_4 group, there are other evidences from crystal data that supports this site assignment (see below). The ideal, fully ordered end-member formula of fluorarrojadite-(BaNa) is $^{A1}Ba^{A2}\square^{B1}Na^{B2}Na^{Ca}Ca^{Na1}Na^{Na2}Na^{Na3}\square^{M}Fe_{13}Al(PO_4)_{11}(PO_3OH)^{W}(F_2)$, which can be simplified as $BaNa_4CaFe_{13}Al(PO_4)_{11}(PO_3OH)F_2$, and requires Na_2O 5.63, BaO 6.97, CaO 2.55, FeO 42.44, Al_2O_3 2.32, P_2O_5 38.69 F 1.73, H_2O 0.41, O=F -0.73, total 100.00 wt.%. Studied holotype material was homogenous, but some of earlier collected samples from Gemerská Poloma studied by Števko *et al.* (2015) suggest that a complete solid solution exists between fluorarrojadite-(BaNa) and arrojadite-(BaNa), following a simple $F^- \leftrightarrow (OH)^-$ substitution. Likewise, a solid solution exists between fluorarrojadite-(BaNa) and an as yet unapproved new member of arrojadite group "fluordickinsonite-(BaNa)".

X-ray diffraction data

Single-crystal X-ray studies of fluorarrojadite-(BaNa) were not carried out because of the absence of suitable single crystals: as studied material is very fine grained (individual grains up to 0.01 mm) and several attempts to obtain suitable single crystal from the fine grained mass of fluorarrojadite-(BaNa) were unsuccessful.

X-ray powder diffraction data of fluorarrojadite-(BaNa) were recorded using a Bruker D8 Advance diffractometer equipped with solid-state LynxEye detector and secondary

monochromator producing Cu$K\alpha$ radiation housed at the Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic. The instrument was operating at 40 kV and 40 mA. In order to minimize the background, the powdered sample was placed on the surface of a flat silicon wafer in ethanol suspension. The powder pattern was collected in the Bragg–Brentano geometry in the range 3-75° 2θ, step 0.01° and counting time of 30 s per step (total duration of experiment was ca. 3 days). Positions and intensities of diffractions were found and refined using the Pearson VII profile-shape function of the ZDS program package (Ondruš, 1993) and the unit-cell parameters were refined by the least-squares program of Burnham (1962). The X-ray powder diffraction data of fluorarrojadite-(BaNa) are given in Table 3. Unit-cell parameters of fluorarrojadite-(BaNa) refined for the monoclinic space group *Cc* are: a = 16.563(1) Å, b = 10.0476(6) Å, c = 24.269(1) Å, β = 105.452(4)°, V = 3957.5(4) Å^3 and Z = 4. Application of Rietveld refinement is highly questionable considering that the structure has > 90 independent atom sites. However, we conducted a test using the collected data and the model published by Cámara et al. (2006) for arrojadite-(SrFe), allowing for refinement of cation occupancies at A1, A2, B1, Na3 and Ca sites (Ba vs. K, Na, Na vs. Fe, Na, Na and Ca vs. Sr, respectively). The chemistry at the M1 and M3 sites was allowed to vary, while was hold fixed in all the other M sites. The atom coordinates of every cation and anion sites in the structure were kept fixed. Refinement was performed with GSAS+EXPGUI software (Larson and Von Dreele, 1994; Toby, 2001). The residuals improved sensibly (wRp = 0.0398, wRp after background subtraction 0.0911; $R(F^2)$ = 0.1475) when chemistry was allowed to vary in the above reported sites. Obviously, the results should interpreted with caution. Nevertheless the trend agrees well with what was expected from the formula obtained on the basis of crystal chemical criteria. Occupancy at M1 was found 18.0(7) eps, as expected for fractionation of Li at this site already found in dickinsonite-(KMnNa) by Cámara *et al.* (2006). Zn seems to order in M3 site that is among the smaller octahedra but yielded 29.1(6)

247 eps, evidently overestimated. The most interesting results are obtained for alkali sites: 48.5(4)
248 vs. 43.1 eps form chemical formula in A1 site; 2.5(8) vs. 3.9 eps from chemical formula in A2
249 site; 25.7(5) vs. 26.3 eps from chemical formula in Ca site; 2.5(8) vs. 3.9 eps from chemical
250 formula in A2 site; 22.8(6) vs. 17.9 eps from chemical formula in B1 site; and 1.2(7) vs. 5.1
251 eps from chemical formula in Na3 site. Therefore the worst agreement are found in the B1
252 and Na3 sites, which are usually split sites (see Cámara *et al*. 2006) thus seriously challenging
253 any plausible satisfactory result. Figure 3 reports the observed and calculated patterns and the
254 relative residuals. The results are a reasonable support of the proposed crystal chemical
255 formula.
256
257
258 **Relationship to the known species and origin**
259 As was mentioned, fluorarrojadite-(BaNa) is a member of the arrojadite group
260 (Cámara *et al.,* 2006; Chopin *et al.,* 2006). Its existence was already noted in samples of
261 fluoarrojadite-(BaFe) from the Sidi Bou Kricha pegmatite in Morocco by Chopin *et al.* (2006)
262 and it was also described as a product of the hydrothermal alteration of triphylite from the
263 Nanping No. 31 granitic pegmatite in Fujian Province, China by Rao *et al.* (2014). The
264 studied sample has a rather high content of Mn^{2+}, among the highest reported for arrojadites
265 in literature. Only the sample from Buranga (Rwanda) (von Knorring, 1969) has an higher
266 Mn content and such it is very close to be classified as dickinsonite. It is not surprising that in
267 the same locality (Gemerská Poloma) some minute crystals showed compositions classifiable
268 as "fluordickinsonite-(BaNa)" (Števko *et al.,* 2015). The Mg content is fairly low (only 0.12
269 *apfu*), lower than in most of the analyses reported for arrojadites, except for arrojadite-(PbFe)
270 coming from Sapucaia (Moore and Ito, 1979) which contains 3.49 *apfu* of Mg and for
271 arrojadite-(BaFe) from Spluga (Demartin *et al.,* 1996) which reaches 5.54 *apfu* of Mg, but

still far from being classifiable as carmoite-(BaFe). Another interesting chemical feature is the presence of significant Li (0.37 *apfu*), not uncommon in arrojadites although far lower than the amount present in arrojadite-(PbFe) from Sapucaia (0.86 *apfu*, data from Cámara *et al.,* 2006).

In the Strunz mineral classification system fluorarrojadite-(BaNa) fits in subdivision 8.BF: phosphates, arsenates, vanadates with additional anions, without H_2O, with medium-sized and large cations and (OH, etc.):$RO_4 < 0.5:1$ (Strunz and Nickel, 2001). The comparison of physical properties of the valid mineral species of the arrojadite subgroup are given in Table 4. The observed lattice parameters are among the largest of the arrojadite subgroup and this is due to the fairly low Mg content. In general, all the cell dimensions are negatively correlated with the Mg content. The value observed for the β angle deviates from the positive trend observed by Cámara *et al.* (2006), which compares the value of the β angle with the (Na+K) content (see their Fig. 1), for samples with vacant Na3 site. This indications is in support of the presence of Na at the Na3 site as suggested by the site assignment on the basis of crystal-chemical criteria and the weak evidence from Rietveld refinement of the presence of some occupation at this site.

Fluorarrojadite-(BaNa) and associated phosphates in quartz veins were formed from late-magmatic to early-hydrothermal P- and F-rich fluids, related to the adjacent granite. These relatively high-temperature fluids altered primary magmatic minerals of the granite (especially albite, K-feldspar, Li-rich micas and fluorapatite) and liberated elements (such as Na, K, Fe, Mn, Ca, Ba, Sr, and P) necessary for precipitation of the phosphate minerals.

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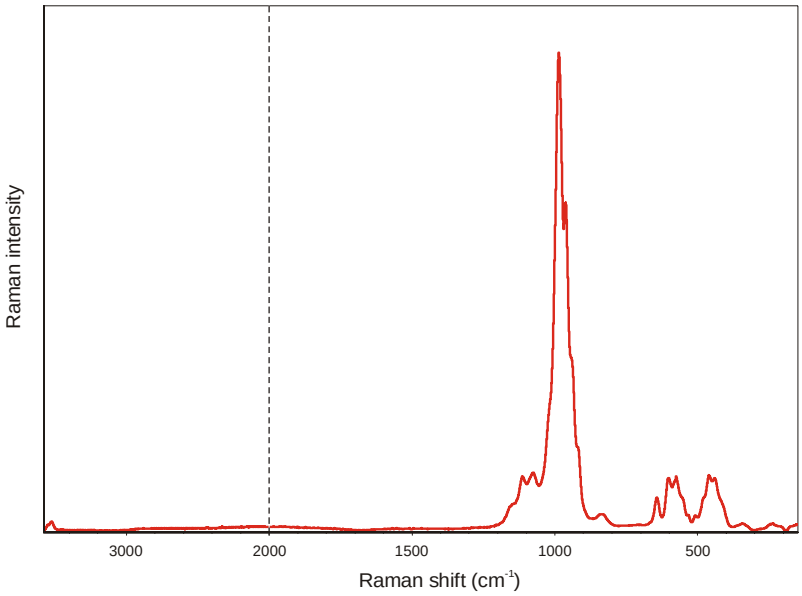
394

FIGURE CAPTIONS

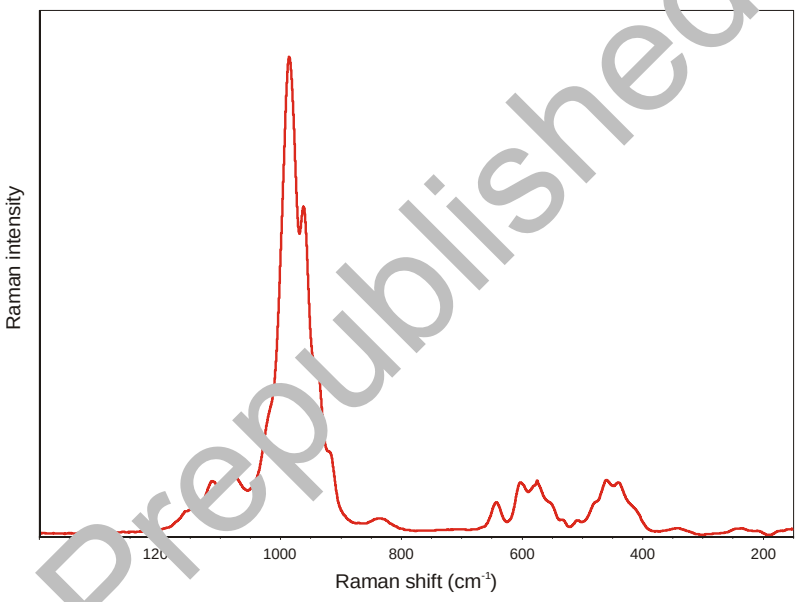
Fig. 1. Yellowish-brown fine grained aggregate of fluoarrojadite-(BaNa) associated with minor dark green grains of fluorapatite in quartz matrix. Field of view is 40 mm. Photographed by Pavel Škácha.



401

402 Fig. 2a. Raman spectrum of fluorarrojadite-(BaNa) from Gemerská Poloma, full range.

403

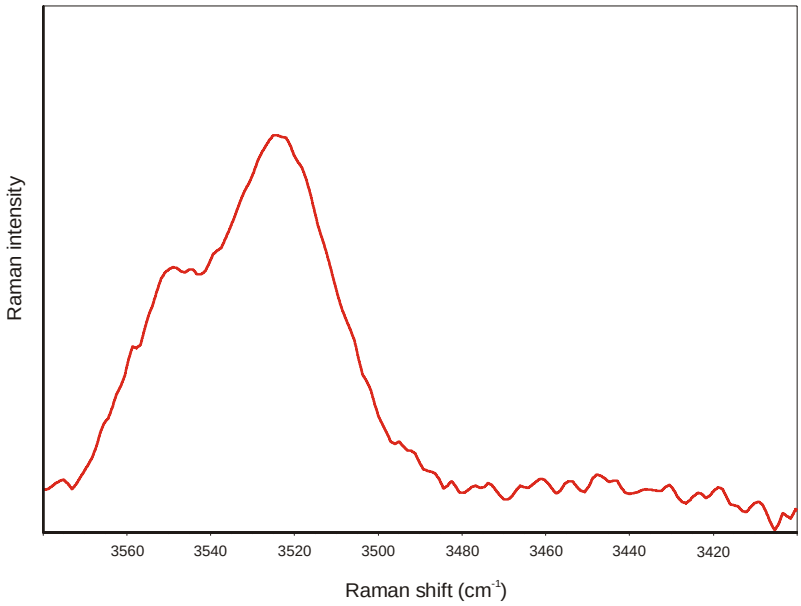


404

405 Fig. 2b. Raman spectrum of fluorarrojadite-(BaNa) from Gemerská Poloma, range 150 – 1400

406 cm^{-1}.

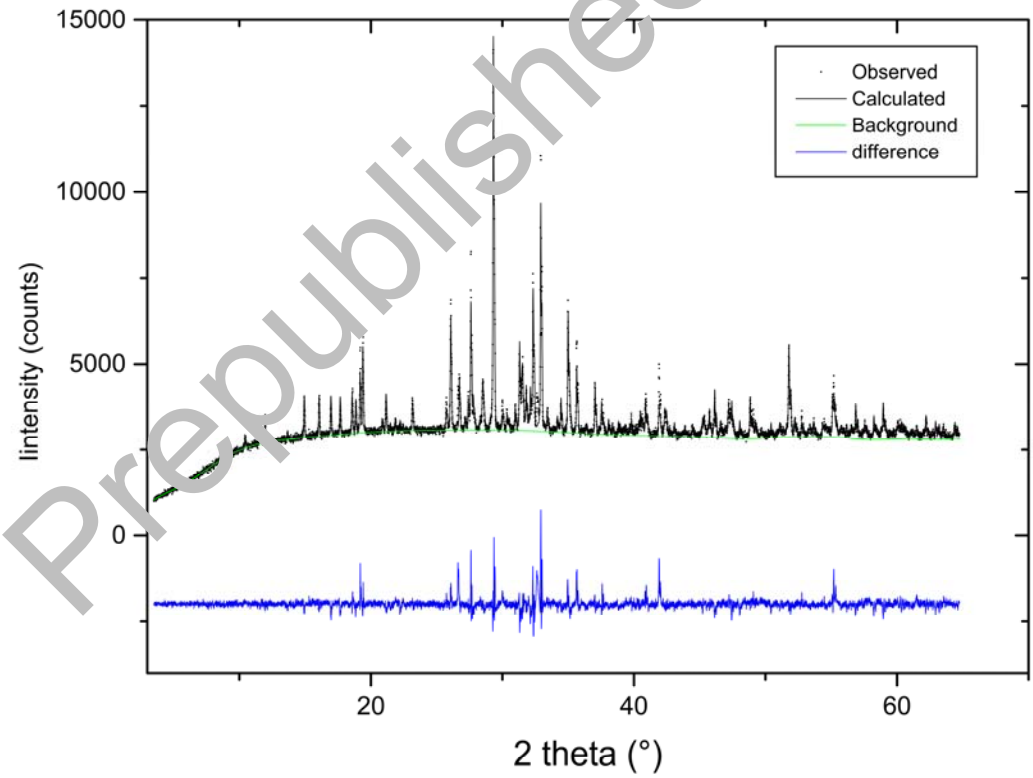
407



408

409 Fig. 2c. Raman spectrum of fluorarrojadite-(BaNa) from Gemerská Poloma, range 3400 –

410 3580 cm^{-1}.



411

412 Figure 3. Observed powder pattern of fluorarrojadite-(BaNa). The calculated intensities,

413 substracted background and residuals obtained by Rietveld refinement (see text) are also

414 reported.

Table 1. Chemical composition (in wt%) of fluorarrojadite-(BaNa).

Constituent	Mean	Range	SD	Standard
K_2O	0.76	0.70 - 0.86	0.07	sanidine
Na_2O	5.72	5.52 - 5.84	0.36	albite
Li_2O*	0.26	0.26		NIST SRM 610
BaO	4.91	4.02 - 5.73	0.18	baryte
SrO	0.98	0.70 - 1.36	0.18	$SrSO_4$
CaO	1.93	1.85 - 2.01	0.08	fluorapatite
PbO	0.23	0.12 - 0.38	0.12	vanadinite
MgO	0.23	0.21 - 0.24	0.03	Mg_2SiO_4
ZnO	0.22	0.19 - 0.24	0.11	gahnite
MnO	17.08	16.86 - 17.32	0.46	spessartine
FeO	25.51	25.21 - 26.15	0.55	almandine
Al_2O_3	2.43	2.31 - 2.50	0.09	sanidine
Sc_2O_3*	0.26	0.26		NIST SRM 610
Ga_2O_3*	0.08	0.08		NIST SRM 610
TiO_2	0.07	0.05 - 0.10	0.02	titanite
P_2O_5	39.75	39.21 - 40.26	0.5	fluorapatite
F	1.36	1.30 - 1.46	0.11	topaz
H_2O**	0.47			
O=F	-0.57			
Total	101.67			

* obtained by LA-ICP-MS

** calculated as (F+OH+Na3) = 3 *apfu*

Table 3. X-ray powder diffraction data of fluorarrojadite-(BaNa) from Gemerská Poloma; the strongest diffractions are reported in bold.

$I_{meas.}$	$d_{meas.}$	$d_{calc.}$	h	k	l	$I_{meas.}$	$d_{meas.}$	$d_{calc.}$	h	k	l	$I_{meas.}$	$d_{meas.}$	$d_{calc.}$	h	k	l
1	8.506	8.504	1	1	0	12	2.5959	2.5965	1	3	-6	9	1.7577	1.7579	6	4	2
2	7.638	7.634	2	0	-2	**33**	**2.5563**	**2.5583**	**0**	**2**	**8**	4	1.7551	1.7563	8	0	4
3	7.436	7.433	1	1	-2	**33**	**2.5563**	**2.5558**	**4**	**2**	**4**	4	1.7551	1.7551	7	1	6
1	6.494	6.495	1	1	2	8	2.5447	2.5446	6	0	-6	3	1.7287	1.7288	6	2	-12
5	5.940	5.945	0	0	4	**23**	**2.5117**	**2.5119**	**0**	**4**	**0**	1	1.7149	1.7146	3	5	-7
4	5.527	5.524	2	0	-4	5	2.4204	2.4202	4	2	-8	1	1.7135	1.7138	5	5	-1
5	5.235	5.233	1	1	-4	9	2.4181	2.4175	6	2	-2	1	1.7135	1.7130	1	1	-14
6	5.023	5.024	0	2	0	7	2.3875	2.3870	6	2	-4	2	1.7104	1.7099	4	4	-10
7	4.775	4.774	3	1	-2	2	2.3570	2.3570	3	1	-10	4	1.7008	1.7008	5	[illegible]	0
5	4.704	4.703	3	1	0	3	2.3377	2.3375	6	2	-5	3	1.6819	1.6819	1	5	[illegible]
11	4.627	4.628	0	2	2	1	2.3118	2.3111	5	3	0	2	1.6788	1.6787	5	1	10
14	4.577	4.578	1	1	4	1	2.2970	2.2970	1	3	7	2	1.6749	1.6750	5	[illegible]	[illegible]
2	4.253	4.252	2	2	0	1	2.2641	2.2635	4	2	-9	8	1.6606	1.6603	3	5	-8
5	4.198	4.200	3	1	-4	3	2.2568	2.2565	5	3	-5	8	1.6606	1.6605	2	2	-14
1	4.196	4.197	2	2	-2	8	2.1985	2.1983	7	1	-6	3	[illegible]	1.6582	0	6	2
1	4.128	4.130	4	0	-2	5	2.1494	2.1494	0	2	10	3	1.[illegible]52	1.6579	8	2	4
2	4.058	4.059	3	1	2	4	2.1458	2.1461	4	4	-2	5	1.65[illegible]7	1.6563	1	3	12
1	3.962	3.963	0	0	6	5	2.1268	2.1260	4	4	0	2	1.6308	1.6310	1	5	8
6	3.837	3.837	0	2	4	3	2.1218	2.1217	0	4	6	[illegible]	1.6223	1.6222	3	1	-15
6	3.837	3.835	2	2	2	3	2.0910	2.0906	7	1	2	4	1.6223	1.6222	1	1	14
1	3.542	3.544	2	2	3	2	2.0554	2.0549	7	[illegible]	[illegible]	8	1.6124	1.6124	4	0	12
1	3.512	3.513	4	0	2	3	2.0295	2.0296	[illegible]	2	4	2	1.5939	1.5944	10	0	-8
5	3.457	3.458	3	1	-6	7	1.9942	1.9958	8	[illegible]	0	2	1.5939	1.5936	7	1	8
5	3.457	3.454	0	2	5	8	1.9770	1.9771	[illegible]	5	-2	5	1.5770	1.5770	6	0	10
21	**3.412**	**3.412**	**1**	**1**	**6**	11	1.9601	1.9606	2	2	10	2	1.5615	1.5626	8	4	0
12	3.328	3.328	3	1	4	1[illegible]	[illegible].960	1.9597	4	2	8	3	1.5596	1.5602	8	2	-12
2	3.277	3.278	1	3	0	3	1.9429	1.9428	2	4	-8	3	1.5596	1.5589	10	2	-6
2	3.271	3.271	1	3	-1	1	1.9288	1.9287	7	3	-2	6	1.5336	1.5335	4	6	-4
6	3.247	3.248	2	2	4	2	1.9255	1.9258	7	1	4	2	1.5268	1.5269	7	5	-4
37	**3.224**	**3.225**	**2**	**0**	[illegible]	3	1.9204	1.9201	3	3	8	2	1.5268	1.5268	10	0	-10
8	3.205	3.205	1	[illegible]	[illegible]	3	1.9190	1.9186	0	4	8	1	1.5197	1.5197	10	2	-8
10	3.126	3.129	2	[illegible]	-6	4	1.9180	1.9176	4	4	4	1	1.5197	1.5196	8	4	-8
10	3.126	[illegible]124	3	1	-7	8	1.9086	1.9085	8	0	-8	4	1.4863	1.4866	5	5	-10
100	**3.0[illegible]0**	**3[illegible]89**	**4**	**2**	**-4**	3	1.8852	1.8852	7	3	0	4	1.4863	1.4862	2	6	6
5	2.972[illegible]	[illegible].9726	0	0	8	7	1.8580	1.8583	4	4	-8	3	1.4698	1.4703	9	1	-13
3	2.9386	2.9[illegible]91	1	3	-4	7	1.8580	1.8571	6	4	-2	3	1.4698	1.4691	11	1	-7
1	2.9226	2.9216	5	1	-5	1	1.8436	1.8443	5	3	-10	3	1.4698	1.4694	2	2	-16
4	2.8791	2.8788	4	2	2	1	1.8436	1.8431	6	4	-4	3	1.4638	1.4633	10	2	2
22	**2.8499**	**2.8499**	**3**	**3**	**-2**	2	1.8428	1.8429	1	1	-13	2	1.4589	1.4590	0	6	8
18	2.8327	2.8346	3	3	0	2	1.8428	1.8412	6	0	-12	2	1.4589	1.4585	4	6	4
1	2.8308	2.8312	3	1	-8	1	1.8265	1.8277	7	3	-7	2	1.4411	1.4411	2	4	-14
11	2.8062	2.8064	1	3	4	1	1.8265	1.8266	6	4	0	2	1.4318	1.4318	4	0	14
9	2.7782	2.7778	5	1	-6	3	1.8019	1.8017	7	3	2	2	1.4294	1.4295	1	5	-12
17	2.7619	2.7618	4	0	-8	2	1.7799	1.7799	9	1	-6	2	1.4294	1.4295	4	4	-14
11	2.7580	2.7579	6	0	-2	2	1.7799	1.7795	8	0	-10	5	1.4253	1.4250	6	6	-4
56	**2.7135**	**2.7138**	**2**	**2**	**6**	1	1.7721	1.7718	4	4	6	5	1.4253	1.4252	0	2	16
5	2.6732	2.6733	3	3	2	14	1.7596	1.7596	2	4	-10	4	1.4236	1.4235	8	2	8
3	2.6166	2.6165	2	2	-8	14	1.7596	1.7594	2	0	-14	1	1.4145	1.4156	6	2	-16

Table 2. Trace element LA-ICP-MS analyses of fluorarrojadite-(BaNa) from Gemerská Poloma (in ppm).

Spot #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Average	Det. limit
Li	1178	1204	1203	1347	1200	1076	1106	1424	1293	1283	1155	1081	20[illegible]	1143	942	1189	0.2
Be	2.2	2.9	2.2	3.5	2.5	1.9	2.6	2.3	2.2	2.1	3.9	3.0	2.[illegible]	3.1	2.3	2.6	0.1
B	10	9.0	8.5	10	9.3	6.7	8.2	12	6.5	6.0	5.7	5.[illegible]	[illegible].5	6.5	4.8	7.7	1.6
Sc	1458	1384	1483	1150	1146	1885	1656	2183	1754	1741	1258	14[illegible]	1944	2081	1755	1623	0.2
Ti	299	367	337	328	310	285	273	360	339	302	292	2[illegible]	336	315	284	314	0.4
V	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	0.1
Cr	1.4	<	1.3	1.9	0.6	<	<	1.0	<	<	2.4	0.6	<	<	<	1.3	0.3
Co	0.5	0.4	0.4	3.1	0.5	0.2	0.4	0.6	0.7	0.5	[illegible].4	0.3	0.4	0.3	0.4	0.6	0.1
Cu	2.3	1.6	1.7	2.6	2.0	2.2	1.8	3.6	2.1	2.2	1.6	2.0	3.3	2.7	2.5	2.3	0.3
Ga	541	545	693	560	562	642	609	709	621	636	511	524	555	673	621	600	0.1
Ge	64	67	73	62	63	54	53	59	49	[illegible]	47	41	41	44	39	53	0.1
Rb	47	57	57	73	53	34	39	49	59	45	71	56	50	35	37	51	0.1
Y	14	19	17	19	17	11	14	16	17	[illegible].4	17	17	14	16	14	16	0.1
Zr	0.7	0.9	0.7	1.0	0.8	0.6	0.8	0.9	0.[illegible]	0.6	0.9	0.8	0.8	0.6	0.7	0.8	0.1
Nb	0.7	1.1	0.4	0.6	0.6	0.6	0.6	0.8	[illegible].8	0.5	0.5	0.5	0.6	1.2	0.9	0.7	0.1
Sn	3.0	0.4	<	<	<	<	<	<	<	<	<	0.2	<	2.1	1.1	1.4	0.1
Sb	0.5	0.5	0.5	0.9	0.7	0.5	0.4	0.[illegible]	0.5	0.7	0.5	0.5	0.5	0.9	0.5	0.6	0.1
La	1.8	1.1	1.2	1.1	1.0	0.8	0.9	[illegible].0	1.0	1.0	0.7	0.9	0.9	0.8	0.8	1.0	0.1
Ce	4.8	2.8	3.3	3.5	3.2	2.1	2.7	2.8	2.7	2.5	2.5	2.2	2.3	2.3	2.2	2.8	0.1
Pr	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	0.1
Nd	1.3	0.8	1.0	1.3	1.2	0.5	[illegible].8	[illegible].0	0.9	0.6	0.6	0.6	0.7	0.7	0.5	0.8	0.1
Sm	0.5	0.3	0.5	0.4	0.4	0.3	0.[illegible]	0.6	0.4	0.4	0.2	0.3	0.3	0.3	0.4	0.4	0.1
Eu	3.5	2.9	3.5	3.2	3.2	2.8	[illegible].5	3.6	2.8	3.3	2.6	2.8	3.1	3.1	3.1	3.1	0.1
Gd	0.6	0.4	0.6	0.7	0.6	0.3	0.[illegible]	0.7	0.5	0.4	0.5	0.4	0.5	0.5	0.5	0.5	0.1
Tb	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	0.1
Dy	1.4	1.6	1.8	1.6	1.8	[illegible].3	1.3	1.8	1.8	1.3	1.6	1.6	1.5	1.4	1.4	1.5	0.1
Ho	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	0.1
Er	1.3	1.6	1.7	1.6	[illegible].5	1.0	1.2	1.4	1.3	1.3	1.2	1.3	1.4	1.3	1.2	1.4	0.1
Tm	0.3	0.4	0.5	0.4	[illegible].4	0.3	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.4	0.3	0.4	0.1
Yb	3.6	4.9	4.6	[illegible].5	4.4	3.0	4.2	4.3	3.7	4.0	3.9	4.0	4.2	4.2	3.6	4.1	0.1
Lu	0.7	0.9	0.9	0.[illegible]	0.9	0.6	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.8	0.1
Th	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	0.1
U	1.1	1.4	1.1	1.9	1.3	1.1	1.3	1.8	0.8	0.8	1.5	1.3	0.9	1.8	1.1	1.3	0.1

Table 4. Comparison of the physical properties for valid members of the arrojadite group (dickinsonites and fluorcarmoite-(BaNa) are not included).

mineral	fluorarrojadite-(BaNa)	fluorarrojadite-(BaFe)	arrojadite-(BaFe)	arrojadite-(KFe)	arrojadite-(KNa)	arrojadite-(PbFe)	arrojadite-(SrFe)	arrojadite-(BaNa)
type locality	Gemerská Poloma, Slovakia	Sidi Bou Kricha, Morocco	Spluga Valley, Italy	Nickel Plate Mine, USA	Rapid Creek, Canada	Sapucaia, Brazil	Horrsjöberg, Sweden	Luna, Dorio, Italy
reference	this work	Chopin *et al.* (2006)	Demartin *et al.* (1996), Chopin *et al.* (2006)	Chopin *et al.* (2006)	Cámara *et al.* (2006)	Chopin *et al.* (2006)	Cámara *et al.* (2006)	Vignola *et al.* (2015)
ideal formula	$(Ba□)(Na)_2Ca(Na_2□)Fe_{13}Al(PO_4)_{11}(PO_3OH)F_2$	$(Ba□)(Fe^{2+}□)Ca(Na_2□)Fe_{13}Al(PO_4)_{11}(PO_3OH)F_2$	$(Ba□)(Fe^{2+}□)Ca(Na_2□)Fe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$	$(KNa)(Fe^{2+}□)Ca(Na_2□)Fe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$	$(KNa)(Na)Ca(Na_2□)Fe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$	$(Pb□)(Fe^{2+}□)Ca(Na_2□)Fe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$	$(Sr□)(Fe^{2+}□)Ca(Na_2□)Fe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$	$BaNa_3(NaCa)Fe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Cc*	*Cc*	*C*2/*c* or *Cc*	*Cc*	*Cc*	*Cc*	*Cc*	*C*2/*c*
a [Å]	16.563(1)	16.4970(9)	16.406(5)	no data	16.5220(11)	16.4304(9)	16.3992(7)	16.4984(6)
b [Å]	10.0476(6)	10.0176(5)	9.945(3)		10.0529(7)	9.9745(5)	9.9400(4)	10.0228(3)
c [Å]	24.669(1)	24.6359(13)	24.470(5)		24.647(16)	24.5869(13)	24.4434(11)	24.648(1)
β [°]	105.452(4)	105.649(2)	105.73(2)		106.509(2)	105.485(2)	105.489(1)	105.850(4)
V [Å^3]	3957.5(4)	3920.42(5)	3843(2)		3932.2(7)	3883.2(5)	3839.76(46)	3921
Z	4	4	4		4	4	4	4
strongest powder X-ray diffractions	3.412/21 3.224/37 3.040/100 2.8499/22 2.7135/56 2.5563/33 2.5117/23	3.4003/31.2 3.2108/47.5 3.0319/100 2.8413/34.1 2.8285/30.0 2.7595/32.9 2.7031/68.5 2.5433/38.1	3.010/100***** 3.178/51 2.678/42 2.523/27 2.805/25 2.775/21 2.741/21 2.732/21	no data	5.8614/28.8 5.0264/27.5 3.1857/33.5 3.0498/100 2.8529/22.4 2.7979/24.9 2.7933/28 2.7532/22.8 2.6908/71.3	4.5534/25.1 3.20882/43.1 3.0186/100 2.8291/35.0 2.8196/32.9 2.7496/29.1 2.6982/54.8 2.5376/30.4	3.3784/26.2 3.2931/21.0 3.1925/41.2 3.0093/100 2.8202/23.5 2.8053/28.4 2.7370/27.8 2.7304/20.1 2.6861/69.9	3.488/28 3.303/46 3.137/100 2.878/32 2.818/61 2.667/35
density	3.650 g.cm^{-3}	3.650 g.cm^{-3}	3.544 g.cm^{-3}	no data	3.437 g.cm^{-3}	3.596 g.cm^{-3}	3.569 g.cm^{-3}	3.76 g.cm^{-3}
colour	yellowish-brown to greenish-yellow	dark yellowish-green	grayish green	dark yellowish-green	yellow	pale honey	green	pale grayish-green

***** data from Demartin *et al.* (1996) for space group *C*2/*c*