



ARROJADITE-(BANA), $\text{BANA}_3(\text{Na}, \text{Ca})\text{Fe}^{2+}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH})(\text{OH})_2$, A NEW PHOSPHATE MINERAL FROM THE LUNA ALBITE PEGMATITE, DORIO COMMUNE, LECCO PROVINCE, ITALY.

^{1,2}Pietro Vignola, ³Frédéric Hatert, ³Maxime Baijot, ³Fabrice Dal Bo, ⁴Sergio Andò, ⁵Danilo Bersani, ²Andrea Risplendente and ²Alessandro Pavese

- ¹ Italian National Council of Researches (CNR), Institute for the dynamics of environmental processes (IDPA), via Botticelli 23 – 20133 MILANO, Italia; # pietro.vignola@idpa.cnr.it, # pietro.vignola@idpa.cnr.it
- ² University of Milano, Department of Earth Sciences “A. Desio”, via Botticelli 23 – 20133 MILANO, Italia
- ³ Laboratoire de Minéralogie, Département de Géologie, Université de Liège, Bâtiment B18, Sart Tilman, B-4000 Liège, Belgique
- ⁴ Dipartimento di Scienze Geologiche e Ambientali, Università Milano-Bicocca, Piazzale della Scienza 4-U4 – 20126 Milano, Italia
- ⁵ Dipartimento di Fisica e Scienze della Terra, Università di Parma, Viale G.P. Usberti 7/a, 43124 Parma, Italia

Key words: arrojadite-(BaNa), new phosphate mineral species, arrojadite group, Luna albite pegmatite, Piona pegmatite swarm, Lecco province, central Southern Alps, Italy

INTRODUCTION

Minerals belonging to the arrojadite group are ubiquitous phosphates occurring in metamorphic, magmatic, and sedimentary environments. Particularly, members of the arrojadite-dickinsonite series, form primary phosphates in granite pegmatites where they occur as masses up to 15 cm in diameter, showing a good cleavage, and colours varying from pale yellow to dark bottle green or brownish. Arrojadite-dickinsonite is typical of Lithium-Cesium-Tantalum (LCT) pegmatites belonging to the beryl-columbite-phosphate subtype in the classification of Černý & Ercit (2005). Recently the crystal-chemistry of this group of phosphates had been reinvestigated by Cámara *et al.* (2006) and Chopin *et al.* (2006) who established the new classification of the group and the following general formula $\text{A}_2\text{B}_2\text{CaNa}_{2-x}\text{M}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH}_{1-x})\text{W}_2$, where A correspond to large divalent cations (Ba, Sr, Pb) and vacancy or monovalent cations (K, Na). B corresponds to small divalent cations (Fe, Mn, Mg) and vacancy or monovalent Na cations. The metal in the M site defines the root name arrojadite (Fe) or dickinsonite (Mn). W site may be occupied by OH or F (arrojadite or fluorarrojadite). This paper presents the mineralogical description of the new species arrojadite-(BaNa) (IMA 2014-071).

OCCURRENCE, GENERAL APPEARANCE, AND PHYSICAL PROPERTIES

Arrojadite-(BaNa) was found in the mine dumps of the Luna albite pegmatite, Dorio commune, Lecco province, Italy. The Luna mining locality, mined for ceramic albite during 1960-1970, consists of three different albite pegmatite dikes belonging to the Late Triassic Piona pegmatite swarm. Arrojadite-(BaNa) occurs as low temperature primary phosphate in the blocky-plagioclase zone as rounded masses or roughly crystallized individuals up to 4-5 cm in diameter hosted by albite. It is frequently associated with fluorapatite. The colour is pale greyish-green, translucent or pale yellowish brown when altered, and the lustre is greasy. The mineral is brittle with an irregular fracture and its Mohs hardness is 4-5 by comparison with the other members of the arrojadite group. A good cleavage was observed on {110}. The specific gravity of 3.531(1) was measured by means of hydrostatic weighting. The calculated density is 3.76 g/cm³. Arrojadite-(BaNa) is biaxial (+), with intermediate dispersion. Its birefringence is low, with first order white or yellow interference colors. Thick grains show a wide range of polarization colors of second order (yellow-mauve-blue). The measured refractive indices are $\alpha = 1.656(2)$, $\beta = 1.660(2)$, and $\gamma = 1.664(2)$. The measured $2V = 40(1)^\circ$ and the calculated one is 45° . The optical axes plane is perpendicular to {110} (cleavage); the angle $Z/c = 17/18^\circ$. Arrojadite-(BaNa) is non fluorescent. The compatibility index, $1 - (K_p/K_c) = -0.013$, superior.

Arrojadite-(BaNa), BaNa₃(Na,Ca)Fe²⁺₁₃Al(PO₄)₁₁(PO₃OH)(OH)₂, a new phosphate mineral from the Luna albite pegmatite, Dorio commune, Lecco province, Italy.

CHEMICAL COMPOSITION

Quantitative averaged chemical analyses, performed on a polished section of arrojadite-(BaNa) using a JEOL JXA-8200 electron microprobe working in wavelength-dispersion mode gave the following empirical formula calculated on the basis of 12 P pfu and with water content calculated considering 2(OH⁻ + F) pfu:

$(\text{Ba}_{0.62}\text{K}_{0.27}\text{Pb}_{0.13}\text{Sr}_{0.07})_{\Sigma 1.09}\text{Na}_3(\text{Na}_{1.19}\text{Ca}_{0.85})_{\Sigma 2.04}(\text{Fe}^{2+}_{9.82}\text{Mg}_{1.92}\text{Mn}^{2+}_{1.64})_{\Sigma 13.38}\text{Al}_{1.01}(\text{PO}_4)_{11}(\text{HPO}_4)(\text{OH}_{1.75}\text{F}_{0.25})_{\Sigma 2}$.

The simplified formula is BaNa₃(NaCa)Fe²⁺₁₃Al(PO₄)₁₁(PO₃OH)OH₂, which requires: BaO 7.07, Na₂O 5.72, CaO 1.29, FeO 43.06, Al₂O₃ 2.35, P₂O₅ 39.72, H₂O 1.25, total 100.00 wt%.

X-RAY DIFFRACTION DATA

The X-ray powder diffraction (XRPD) pattern of arrojadite-(BaNa) has been obtained using a **Panalytical X'pert Pro X-ray powder diffractometer equipped with an X'Celerator-type detector**. Operating conditions were: filtered CuK α radiation, 40 kV, 40 mA, 2 θ -range from 5° to 105°, step size 0.017° 2 θ , counting time 70 s per step. Silicon NIST 640c was used as internal standard. The refined unit-cell parameter for space group C2/c are $a = 15.551(4)$ Å, $b = 10.058(2)$ Å, $c = 24.648(7)$ Å, $\beta = 106.51(2)^\circ$, and $V = 3933(2)$ Å³, for $Z = 4$. The eight strongest measured lines are [d in Å (I/I_0) hkl]: 3.137 (100) 5 1 0, 2.818 (61) 3 1 6, 3.303 (46) -1 3 2, 2.667 (35) 2 0 8, 2.878 (32) 3 3 1, 3.488 (28) 1 1 6, 4.621 (22) -3 1 3, and 2.936 (22) 3 3 0.

The X-ray structural study was carried out on an Agilent Xcalibur 4-circle diffractometer equipped with an EOS CCD detector on a fragment of arrojadite-(BaNa) measuring 0.170 x 0.150 x 0.080 mm. Some 414 frames with a spatial resolution of 1° were collected by the ϕ/ω scan technique, with a counting time of 100 s per frame, in the range $5.83 < 2\theta < 57.44^\circ$. A total of 16452 reflections were extracted from these frames, corresponding to 4608 unique reflections. Unit cell parameters refined from these reflections are in good agreement with those refined from the X-ray powder data $a = 16.4984(6)$ Å, $b = 10.0228(3)$ Å, $c = 24.648(1)$ Å, $\beta = 105.850(4)^\circ$, and $V = 3920.8(2)$ Å³, $Z = 4$, space group C2/c. Data were corrected for Lorenz, polarisation and absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED package. The crystal structure of arrojadite-(BaNa) was refined using, as starting atomic coordinate, those of arrojadite-(BaFe) (previously sigismundite; Demartin *et al.*, 1996). In the final refinement cycle, all atoms, except Na occurring on the X4 site, were refined anisotropically, leading to the R_1 value 0.0581. The crystal structure of arrojadite-(BaNa) is similar to that of arrojadite-(BaFe) (Demartin *et al.*, 1996), with the X2 to X4 sites occupied by Na, the X5 site occupied by Ba, and the M2 to M7 sites occupied mainly by Fe²⁺.

DISCUSSION

Arrojadite-(BaNa) belongs to the arrojadite group, arrojadite subgroup (Dana classification 41.07.02, Anhydrous phosphates containing hydroxyl or halogen – arrojadite group – arrojadite subgroup. Strunz classification 08.BF.05, Phosphates, arsenates vanadates, with additional anions, without H₂O, with medium-sized and large cations), and correspond to the Ba- and Na-rich member of the arrojadite group. Arrojadite-(BaNa) corresponds to the Na-rich analogue of arrojadite-(BaFe) (ex sigismundite, see Demartin *et al.* 1996 and Chopin *et al.* 2006).

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