

## The arrojadite enigma: II. Compositional space, new members, and nomenclature of the group

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### ABSTRACT

A systematic chemical and structural investigation of arrojadite-group minerals has provided new data allowing us to design a consistent nomenclature scheme, approved by the IMA CNMMN (vote 05-D). The cornerstones of this scheme are: (1) the fundamental structural formula for the arrojadite group is  $A_2 B_2 Ca Na_{2+x} M_{13} Al (PO_4)_{11} (PO_3OH_{1-x}) W_2$ , where A are either large divalent cations (Ba, Sr, Pb) plus vacancy, or monovalent (K, Na) cations, B are either small divalent cations (Fe, Mn, Mg) plus vacancy, or monovalent (Na) cations. (2) The dominant cation at the M sites defines the root-name: Fe<sup>2+</sup>, arrojadite; Mn<sup>2+</sup>, dickinsonite; Mg (if any), name to be proposed. (3) Two suffixes are added to the root-name according to the dominant cation of the dominant valence state at the A1 and B1 sites (the mono- or divalent nature of the cation used implicitly specifies the dominant occupancy by Na or the dominant vacancy, respectively, at the A2 and B2 sites, according to two heterovalent substitutions). (4) A third suffix is added in case the sum of non-(P,Al) cations exceeds 20.5 apfu [which implies that the Na3 site is more than half occupied and the total (OH,F) content is less than 2.5 apfu]. (5) Prefixes may be added to the root-name in the case of dominance of F over OH at the W site or of Fe<sup>3+</sup> over Al at the Al site.

The compositional range explored is quite large, with either K, Sr, Ba, or Pb as the dominant cation at A1; Na, Fe, or Mn dominant at B1; Na or vacancies dominant at A2 and B2; Na or vacancy at the Na3 site; and F or OH at the W site. Lithium can amount up to 1 Li pfu and is partitioned into the M sites, preferentially M1. As a consequence of this new nomenclature scheme, the mineral name “sigismundite” is abolished and the corresponding composition must be referred to as arrojadite-(BaFe). In addition, arrojadites–dickinsonites from classic localities are identified as arrojadite-(KFe) (Nickel Plate Mine), dickinsonite-(KMnNa) (Branchville), fluorarrojadite-(BaFe) (Sidi-bou-Kricha), and we define the new members arrojadite-(KNa) (Rapid Creek), arrojadite-(PbFe) (Sapucaia), and arrojadite-(SrFe) (Horrnsjöberg).

**Keywords:** Crystal structure, arrojadite, analysis, chemical (mineral), new minerals, arrojadite-(PbFe), fluorarrojadite-(BaFe), arrojadite-(BaFe), optical properties, XRD data

### INTRODUCTION

“Arrojadites are the most chemically complex of primary pegmatite phosphates, and no less than sixteen elements may play a significant role.” This sentence introduces the discussion given by Moore and Ito (1979) of a chemical survey of available analyses, i.e., those restricted to pegmatitic material. Indeed, arrojadite-group minerals have been considered as confined to granitic pegmatites for a century, until the discoveries of the 1970s in northwestern Yukon Territory, Canada. In these now classic occurrences, crystals of exceptional quality occur in hydrothermal veins cross cutting shale and ironstone of very low metamorphic grade (Robinson et al. 1992). This finding and more recent ones in greenschist- to amphibolite-facies metamorphic quartzites [by Demartin et al. (1996) in the Central Alps and by one of us in south-central Sweden] indicate that the formation conditions of arrojadite-group minerals may be much more diverse than anticipated, as also suggested by the

low-temperature (450 °C) synthesis of a ferrian arrojadite phase (Yakubovich et al. 1986). As a matter of fact, these new findings also reveal large compositional variations, which may, or may not, be related to the broad range of pressures and temperatures of formation now recognized for this mineral. Our analytical and structural study of the Swedish and Canadian samples prompted a re-investigation of classic material. Together with new structural data presented in Part I (Cámara et al. 2006), the results imply complete reconsideration of the crystal chemistry of the arrojadite group; on this basis, we propose in the following a consistent nomenclature scheme, the application of which led to the definition or re-definition of several new members.

### HISTORICAL: ARROJADITE, DICKINSONITE, AND SIGISMUNDITE

The name dickinsonite had been proposed initially to define a phosphate mineral containing Mn, Fe, and Na in the Branchville pegmatite, Fairfield Co., Connecticut (Brush and Dana 1878), and the name arrojadite was proposed by Guimarães (1924, republished by Guimarães 1942, with minor correction of the

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optical data) to define a phosphate mineral containing Fe, Mn, and Na found in the Serra Branca pegmatite, Picuí, Paraíba, Brazil. Mason (1941) suggested that Serra Branca arrojadite may be identical with a similar phosphate mineral long known from the Nickel Plate pegmatite, Keystone, Pennington Co., South Dakota (Headden 1891). The suggestion was confirmed by Lindberg (1950) by direct comparison of the two materials, thereby establishing the precedence of arrojadite over "headdenite," a name that Quensel (1937) introduced in between for the Nickel Plate Mine material. Fisher (1954, 1965) established that dickinsonite and arrojadite are the Mn-dominant and Fe-dominant members of the same series. Von Knorring (1969) analyzed and Huvelin et al. (1972) gave a detailed description of "arrojadite baryfère" from Rwanda and Morocco, respectively, and mentioned a similar finding by Miss M. Mrose in one of the New Hampshire pegmatites. Huvelin et al. (1972) also recognized that the small but consistent  $\text{Al}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ , and, to some extent,  $\text{Li}_2\text{O}$  contents in the analyses are real and essential constituents of arrojadite and dickinsonite. These features were confirmed by Moore and Ito (1979), who provided new analyses from classic and new localities (Minas Gerais; New Hampshire; South Dakota). Then came the time of structural studies, the main episodes of which are told in Part I. After the landmark paper of Moore et al. (1981) in which the ideal formula  $\text{KNa}_4\text{Ca}(\text{Fe},\text{Mn})_{14}\text{Al}(\text{OH})_2(\text{PO}_4)_{12}$  was proposed for the arrojadite–dickinsonite series, Robinson et al. (1992) published electron-microprobe (EMP) analyses of Yukon arrojadites, confirming the existence of a Ba-dominant member and suggesting the occurrence of new  $\text{Fe}^{3+}$ -dominant and F-dominant members. A new occurrence of Ba-dominant (and Mg-rich) arrojadite was found at Spluga, Italian Central Alps, for which the name sigismundite was introduced by Demartin et al. (1996), who emphasized the replacement of K + Na by Ba + □.

### MATERIAL STUDIED

To understand the details of the crystal chemistry of this complex phosphate group, we carried out a systematic study of a new Sr-analog of arrojadite found at Horrsjöberg, south-central Sweden, and on other arrojadite samples from different localities, obtained through curators and colleagues, and thought to represent the chemical diversity of the group. We re-analyzed the sigismundite holotype sample from Spluga (Demartin et al. 1996), samples from the Nickel Plate Mine (Lindberg 1950; Merlino et al. 1981), the Smith Mine, Chandler's Mills, the Victory Mine, Sapucaia, Branchville (Moore and Ito 1979), Yukon Territory (Rapid Creek and Blow River, cf. Robinson et al. 1992; Steele 2002), Sidi-bou-Kricha (Huvelin et al. 1972), and Hagendorf, and did new structure refinements for nearly all of them. We also measured Li (in some selected cases also Be and B) in situ via LA-ICP-MS analysis. The complete chemical analyses are reported in Table 1, together with locality and sample-origin data; analytical details are given in Part I (Cámara et al. 2006). Optical data were measured on samples (proposed as new members of the arrojadite group) from three localities for which no such data were available.

The Horrsjöberg sample was analyzed in examined thin section, from which two crystals were drilled out for X-ray and optical work; for all other specimens, crystals were hand-picked from a gently ground fragment, some mounted in epoxy

for electron-microprobe (EMP) and LA-ICP-MS analyses, and some reserved for X-ray work. The crystals studied by X-ray diffraction were subsequently mounted in epoxy and analyzed in the same way as the others.

This set of occurrences covers some impressive compositional variations (in wt%): 0–5.7 BaO, 0–4.6 SrO, 0–5.3 PbO, 0–0.7  $\text{Li}_2\text{O}$ , 0.1–1.9  $\text{K}_2\text{O}$ , 4.4–7.8  $\text{Na}_2\text{O}$ , 0.1–10.8 MgO, whereas those concerning  $\text{Al}_2\text{O}_3$  (2.0–2.7) and CaO (1.6–2.7 in EMP analyses) are more limited.

### THE CRYSTAL-CHEMICAL BASIS FOR NOMENCLATURE

The main new structural and crystal-chemical features resulting from this work are addressed in Part I (Cámara et al. 2006) and can be summarized as follows, first adapting the site nomenclature used by Moore et al. (1981) to the new structural model (e.g., by adding a and b for the couples of sites that are no longer equivalent when passing from the  $C2/c$  to  $Cc$  space group and adopting the name of the most similar formerly partially occupied X site).

(1) The real space group of the arrojadite series is  $Cc$ . The lowering in symmetry implies recognition of strong cation ordering among the resulting 22 cationic sites beside the 12 independent  $\text{PO}_4$  groups.

(2) There are one octahedral Al site and 13 independent M sites, which are sixfold- or fivefold-coordinated and occupied by Fe, Mg, Mn, and minor Li and Zn.

(3) There are eight independent larger-size X sites, three of which may be vacant (depending on composition, as explained below), and some of which may split into three distinct sub-sites according to the nature of the cations.

(4) The number of OH groups pfu is generally 3 and not 2, but can decrease down to 2 when the X7 site is fully occupied.

Chemical analysis of arrojadite-group minerals is a challenge. Even with a careful choice of standards and analytical procedures, a detailed understanding of the operative chemical exchanges is hampered by the very large formula unit (50 O + F) and by the uncertainty on P, the most abundant and highly charged element, which contributes as much charge as involved in the several heterovalent substitutions. Therefore, a rational scheme for cation incorporation was defined by comparative crystal-chemical analysis mainly based on the results of the structure refinement, namely the geometry and coordination number of the various sites, the refined site-scattering values and the presence or absence of split and/or solid-solution sensitive sites. The following results form the cornerstones of arrojadite crystal chemistry.

(1) No Be or B substituting for P has been detected in the analyzed samples.

(2) The octahedral Al site is occupied by trivalent cations, and Al is always the dominant (often, the only) cation; besides  $\text{Fe}^{3+}$ , minor Sc and  $\text{Ti}^{4+}$  also have been found in a few samples.

(3) The M sites have different coordination geometries and numbers (5–6), and are occupied by divalent cations (Fe, Mn, Mg, Zn) and by minor Li. The Li contents could be measured reliably in situ by LA-ICP-MS analysis (Table 1). Comparison of the observed aggregate site-scattering values at the M and X sites with those calculated from the unit formulae indicate that Li occurs at the M sites and does not distribute among the X sites but between the M1 (preferentially) and the M2a, M6a, M7a

TABLE 1. Chemical analyses and unit-formulae calculation for arrojadite samples

Museum code.	New analyses (EMP + LA-ICP-MS, this work)										
	ENSMP 41081	Fontan	Fontan	Gentile 154	ENSMP 38431	ENSMP 16926	ENSMP 1235	MNHN 167.275	ENSMP 4861	ENSMP 32088	ENSMP 38435
Locality	Yukon, Territory Rapid Creek	Sidi bou Kricha	Sidi bou Kricha	Spluga	Nickel Plate mine	Horrnsjöberg	Victory mine	Nickel Plate mine	Branchville	Sapucaia	Yukon Territory, Blow River
	mean (9)	mean (9)	mean (7)	mean (9)	mean (7)	mean (11)	mean (7)	mean (3)	mean (11)	mean (4)	mean (6)
SiO <sub>2</sub>	nil	0.04	0.06	0.02	0.03	0.06	0.02	0.02	0.02	0.11	nil
BeO <sub>LAM</sub>	nil	0.001	0.001	nil	0.001	n.d.	nil	0.001	nil	nil	nil
B <sub>2</sub> O <sub>3LAM</sub>	nil	0.001	0.001	0.001	nil	n.d.	0.001	0.001	nil	nil	0.001
P <sub>2</sub> O <sub>5</sub> *	41.40	39.12	38.87	41.75	40.70	41.00	40.25	40.20	38.60	40.00	41.30
Al <sub>2</sub> O <sub>3</sub>	2.52	2.34	2.35	2.53	2.42	2.46	2.40	2.45	2.06	2.30	2.44
Fe <sub>2</sub> O <sub>3</sub>									0.40	0.15	
TiO <sub>2</sub>	0.05	nil	nil	nil	0.05	0.01	0.02	0.11	0.04	0.03	0.06
Sc <sub>2</sub> O <sub>3</sub>	nil	n.d.	n.d.	0.02	nil	0.14	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	32.42	27.03	27.16	26.55	28.48	22.94	37.76	28.89	12.63	18.78	32.01
MnO	3.41	13.40	12.91	0.59	14.56	11.34	4.40	13.54	29.75	13.70	5.11
ZnO	n.d.	0.26	0.19	n.d.	0.40	0.28	0.16	0.40	0.03	0.19	0.10
MgO	5.28	1.57	1.52	10.60	1.37	7.00	1.28	1.28	0.11	6.64	4.81
Li <sub>2</sub> O <sub>LAM</sub>	0.005	0.12	0.33	0.29	0.26	0.006	0.001	0.124	0.255	0.606	0.002
Na <sub>2</sub> O	7.73	5.23	4.99	5.68	6.16	4.77	6.98	6.21	7.82	4.60	7.57
K <sub>2</sub> O	1.87	0.62	0.59	0.25	1.71	0.06	1.92	1.76	1.26	0.66	1.83
CaO	2.70	2.20	2.25	2.10	2.51	1.58	2.70	2.56	1.71	2.15	2.46
SrO	0.07	1.00	0.81	1.21	0.06	4.63	0.02	0.11	0.47	0.45	0.05
BaO	0.02	4.15	4.39	5.53	0.12	1.48	0.13	0.07	0.05	2.01	0.02
PbO	0.03	1.02	0.69	0.77	0.20	0.29	0.05	0.10	0.03	5.29	0.07
F	0.01	0.91	0.89	0.66	0.75	0.82	0.33	0.66	0.01	0.53	0.03
H <sub>2</sub> O*	1.31	0.81	0.81	1.01	0.94	0.92	1.12	0.96	1.01	1.02	1.30
TOTAL	98.83	99.82	98.81	99.56	100.72	99.79	99.54	99.45	96.26	99.22	99.16
-O = F	0.00	0.38	0.38	0.28	0.32	0.35	0.14	0.28	0.00	0.22	0.01
TOTAL	98.83	99.44	98.43	99.28	100.40	99.44	99.40	99.17	96.26	99.00	99.15
P <sub>2</sub> O <sub>5</sub> (or.)	41.20	38.62	38.71	41.24	39.56	40.74	39.79	39.94	39.37	39.76	40.90
Si	0.00	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.04	0.00
Be		0.001	0.001		0.001			0.001			
B		0.001	0.001	0.001			0.001	0.001			0.001
P	12.00	11.99	11.98	11.99	11.99	11.98	11.99	11.99	11.99	11.96	12.00
ΣT	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Al	1.02	1.00	1.01	1.01	0.99	1.00	1.00	1.02	0.89	0.96	0.99
Fe <sup>3+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.04	0.00
Ti	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.03	0.01	0.01	0.01
Sc				0.01		0.04					
Fe <sup>2+</sup>	9.28	8.18	8.27	7.53	8.28	6.62	11.11	8.51	3.87	5.54	9.18
Mn <sup>2+</sup>	0.99	4.11	3.98	0.17	4.29	3.31	1.31	4.04	9.25	4.10	1.48
Zn <sup>2+</sup>	0.00	0.07	0.05	0.00	0.10	0.07	0.04	0.10	0.01	0.05	0.02
Mg	2.69	0.85	0.83	5.36	0.71	3.60	0.67	0.67	0.06	3.49	2.46
Li	0.01	0.17	0.48	0.39	0.37	0.01	0.00	0.18	0.38	0.86	0.00
ΣM	12.97	13.38	13.61	13.45	13.75	13.61	13.13	13.50	13.57	14.04	13.14
Na	5.13	3.67	3.52	3.74	4.15	3.19	4.76	4.24	5.57	3.15	5.03
K	0.82	0.29	0.27	0.11	0.76	0.03	0.86	0.79	0.59	0.30	0.80
Ca	0.99	0.85	0.88	0.76	0.94	0.58	1.02	0.96	0.67	0.81	0.90
Ba	0.00	0.59	0.63	0.74	0.02	0.20	0.02	0.01	0.01	0.28	0.00
Sr	0.01	0.21	0.17	0.24	0.01	0.93	0.00	0.02	0.10	0.09	0.01
Pb	0.00	0.10	0.07	0.07	0.02	0.03	0.00	0.00	0.00	0.50	0.01
ΣX	6.95	5.71	5.54	5.66	5.90	4.96	6.66	6.03	6.94	5.13	6.75
F	0.01	1.04	1.03	0.71	0.82	0.89	0.37	0.74	0.01	0.59	0.03
OH	2.99	1.96	1.97	2.29	2.18	2.11	2.63	2.26	2.48	2.41	2.97
ΣF + OH	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	2.49	3.00	3.00
ΣX + M	19.92	19.09	19.16	19.11	19.65	18.57	19.79	19.53	20.51	19.17	19.89
<sup>M</sup> Fe*	-0.03	0.38	0.61	0.45	0.75	0.61	0.13	0.50	0.57	1.04	0.14
X <sup>1+</sup>	5.95	3.96	3.79	3.85	4.91	3.22	5.62	5.03	6.16	3.45	5.83
X <sup>2+</sup>	1.00	1.75	1.75	1.81	0.99	1.74	1.04	1.00	0.78	1.68	0.92
Li <sub>calc</sub>	0.13	0.12	0.43	0.41	0.35	0.10	0.04	0.33		0.83	0.05
Prefix		Fluor	Fluor								
root-name	arrojadite	arrojadite	arrojadite	arrojadite	arrojadite	arrojadite	arrojadite	arrojadite	dickinsonite	arrojadite	arrojadite
1 <sup>st</sup> suffix	K	Ba	Ba	Ba	K	Sr	K	K	K	Pb	K
2 <sup>nd</sup> suffix	Na	Na	Fe	Na	Fe	Fe	Na	Fe	Mn	Fe	Na
3 <sup>rd</sup> suffix								Na			

Notes: Unit formulae calculated according to the procedure given in the text. The original P<sub>2</sub>O<sub>5</sub> content is also reported after the total row.

\* Calculated values.

† Demartin et al. (1996) detected but not measured F; this is the value obtained during this work; Li<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub>, and BeO measured in situ by LA-ICP-MS (estimated accuracy ±10%).

TABLE 1.—Continued

			Old analyses (in the literature; wet chemical unless specified)									
ENSMP 45940 Chandler mills	ENSMP 46953 Smith mine	ENSMP 4859 Smith mine	Lindberg Nickel Plate mine	Huvelin Sidi bou Kricha	Moore and Ito Sapucaia	Moore and Ito Smith mine	Moore and Ito Nancy mine	Moore and Ito Branchville EMP	Moore and Ito Branchville	Moore and Ito Palermo mine	von Knorring Buranga Rwanda	Demartin Spluga EMP
mean (4)			M&I	M&I	M&I	M&I	M&I	M&I no. 9	M&I no. 11	M&I	M&I	Dm et al.
0.06	0.07	0.03										0.02
0.001	0.001	0.001										
nil	nil	nil										
41.85	41.15	40.35	40.90	39.40	41.05	39.60	43.20	40.60	40.15	40.70	39.60	41.3
2.34	2.44	2.49	2.66	2.41	2.23	2.30	2.33	2.00	(2.00)	2.37	1.96	2.45
0.19			0.00	0.00	0.43	0.29	0.39	0.68	0.63	0.10	0.64	0.03
0.06	0.08	0.02										
n.d.	n.d.	n.d.										
28.32	28.98	30.81	28.22	28.05	18.75	28.62	34.55	12.69	12.39	30.00	19.99	27.61
7.57	6.60	6.22	15.78	14.12	14.60	7.43	7.76	32.00	31.83	12.60	19.45	0.70
0.37	0.16	0.34		0.25	0.20	0.17	0.24			0.06		
6.02	5.68	3.99	1.04	1.53	6.78	4.55	3.37			2.49	2.8	10.85
0.356	0.272	0.342	0.09	0.33	0.70	0.25	0.52	(0.17)	0.22	0.08	0.20	
5.65	5.87	5.57	6.40	5.47	4.53	5.50	5.36	7.80	7.37	6.59	4.97	4.44
0.73	1.26	1.16	1.74	0.56	0.58	0.95	1.43	1.10	1.80	1.39	0.63	0.26
2.30	2.70	2.60	2.46	0.82	2.57	2.28	3.65	2.30	2.09	1.31	2.28	2.09
0.28	0.16	0.27		0.31	0.34	0.13	0.05			0.65		1.09
3.70	1.92	2.67		4.32	1.50	2.32	0.02			0.2	5.36	5.68
0.68	1.02	1.01		0.76	4.42	0.88	0.37					0.76
0.41	0.45	0.80	0.80	0.95							0.47	†0.66
1.13	1.10	0.90	0.92	0.80	1.30	1.26	1.37	1.28	1.22	1.29	1.03	1.00
102.02	99.91	99.57	101.01	100.08	99.98	96.53	104.61	100.62	99.70	99.83	99.38	98.94
0.17	0.19	0.34	0.34	0.40							0.20	0.28
101.85	99.72	99.23	100.67	99.68	99.98	96.53	104.61	100.62	99.70	99.83	99.18	98.66
40.55	40.54	39.86	40.00	39.07	41.20	42.30	40.10	39.50	40.89	40.80	39.34	40.50
0.02	0.03	0.01										0.01
0.001	0.001	0.001										
11.98	11.97	11.99	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	11.99
12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
0.93	0.99	1.03	1.09	1.02	0.91	0.97	0.90	0.82	0.83	0.97	0.83	0.99
0.05	0.00	0.00			0.11	0.08	0.10	0.18	0.17	0.03	0.17	0.01
0.02	0.02	0.01										
8.01	8.33	9.04	8.18	8.44	5.41	8.57	9.48	3.70	3.66	8.74	5.98	7.92
2.17	1.92	1.85	4.63	4.30	4.27	2.25	2.16	9.46	9.52	3.72	5.90	0.20
0.09	0.04	0.09		0.07	0.05	0.04	0.06			0.02		
3.03	2.91	2.09	0.54	0.82	3.49	2.43	1.65			1.29	1.49	5.54
0.48	0.38	0.48	0.13	0.48	0.97	0.36	0.69	0.24	0.31	0.11	0.29	0.00
13.78	13.58	13.55	13.48	14.11	14.19	13.65	14.04	13.40	13.49	13.88	13.66	13.66
3.71	3.91	3.79	4.30	3.82	3.03	3.82	3.41	5.28	5.05	4.45	3.45	2.95
0.31	0.55	0.52	0.77	0.26	0.26	0.43	0.60	0.49	0.81	0.62	0.29	0.11
0.83	0.99	0.98	0.91	0.32	0.95	0.87	1.28	0.86	0.79	0.49	0.87	0.77
0.49	0.26	0.37	0.00	0.61	0.20	0.33	0.00	0.00	0.00	0.03	0.75	0.76
0.05	0.03	0.05	0.00	0.06	0.07	0.03	0.01	0.00	0.00	0.13	0.00	0.22
0.06	0.09	0.09	0.00	0.07	0.41	0.08	0.03	0.00	0.00	0.00	0.00	0.07
5.45	5.83	5.80	5.98	5.14	4.92	5.56	5.33	6.63	6.65	5.72	5.36	4.88
0.44	0.49	0.89	0.88	1.08	0.00	0.00	0.00	0.00	0.00	0.00	0.53	0.72
2.56	2.51	2.11	2.12	1.94	3.00	3.00	3.00	2.97	2.86	3.00	2.47	2.28
3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	2.97	2.86	3.00	3.00	3.00
19.23	19.41	19.35	19.46	19.25	19.11	19.21	19.37	20.03	20.14	19.60	19.02	18.54
0.78	0.58	0.55	0.48	1.11	1.19	0.65	1.04	0.40	0.49	0.88	0.66	0.66
4.02	4.46	4.31	5.07	4.08	3.29	4.25	4.01	5.77	5.86	5.07	3.74	3.06
1.43	1.37	1.49	0.91	1.06	1.63	1.31	1.32	0.86	0.79	0.65	1.62	1.82
0.52	0.40	0.57	0.41	0.55	1.01	0.55	0.65	0.19	0.20	0.09	0.28	-0.02
arrojadite	arrojadite	arrojadite	arrojadite	Fluor arrojadite	arrojadite	arrojadite	arrojadite	dickinsonite	dickinsonite	arrojadite	arrojadite	arrojadite
Ba	K	K	K	Na	Na	Pb	K	Na	K	K	Ba	Ba
Fe	Fe	Fe	Na	Fe	Fe	Fe	Fe	Na	Na	Fe	Fe	Fe

Notes: Unit formulae calculated according to the procedure given in the text. The original P<sub>2</sub>O<sub>5</sub> content is also reported after the total row.

\* Calculated values.

† Demartin et al. (1996) detected but not measured F; this is the value obtained during this work; Li<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub>, and BeO measured in situ by LA-ICP-MS (estimated accuracy ±10%).

sites; the exchange vectors responsible for local charge-balance will be discussed in a future contribution.

(4) The X5 site is occupied by a monovalent cation (K, Na) in arrojadites, and a large divalent cation (Ba, Sr, Pb) in sigismundite and the other members; K is generally dominant in arrojadites.

(5) The X4 site is vacant in sigismundite and members rich in Ba, Sr, or Pb, but is filled by Na in other arrojadites.

(6) The fourfold-coordinated (within 3 Å) X6 site is occupied by Na in arrojadites and sigismundite that have about 13 M-type cations (i.e., Fe, Mn, Mg, Li, Zn); in arrojadites and sigismundite with a higher number of M-type cations, this site is progressively substituted by two additional (split) sixfold- and sevenfold-coordinated sites, which are occupied by divalent cations (Ca, Sr) and are locally coupled with vacancy at the adjacent X2a site.

(7) In one locality (Branchville, Cámara et al. 2006), the high number of M-type cations (13.58 apfu) is not compensated by a decrease in the number of X-type cations (6.94 apfu); the structure refinement shows 7.48 epfu at the X7 site, which is close to the position expected for the proton bonded to O3x (whose electron-density maximum is here hardly detectable). Comparative crystal-chemical analysis suggests that the X7 site is occupied mainly by Na (0.52 apfu), with a small amount of Mn (0.11 apfu). This situation is also more suitable to obtain local charge balance after the incorporation of 0.38 Li apfu at some adjacent M sites (e.g., M2, M3, M5, and M6).

(8) In general, Ca is ordered at the X1 sites, whereas heavier cations (e.g., Fe, Ba, Sr) may disorder between the X1 and X6 sites.

### THE MAIN SUBSTITUTIONS INVOLVED

The two samples from the Yukon, which have a relatively simple chemistry close to a nominal arrojadite  $\text{KCaNa}_3(\text{Fe,Mg})_{13}(\text{OH})_2\text{Al}(\text{PO}_4)_{11}\text{PO}_3\text{OH}$  (Table 1), were crucial to define the possible exchange vectors ruling the crystal chemistry of this group of minerals. Starting from this formula, with 13 M-type cations (i.e., Fe, Mn, Mg, Zn, Li) and 7 X cations, the relevant crystal chemical exchanges revealed by the data in Table 1 are an increase of the number of M-type cations (up to 14), a decrease of the number of X-type cations (down to 5) and variations of the number of (M + X) cations from 20 down to 18.6 or up to 20.6 (in the Branchville sample). On the basis of the structural data, these compositional variations can be rationalized through a small number of independent exchange vectors.

(1) Arrojadite and dickinsonite differ because of the homovalent  $\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+}$  exchange at the M sites.

(2) Arrojadite and its Ba, Sr, or Pb varieties differ because of the coupled heterovalent exchange  $^{\text{X5}}\text{K}^+ \text{X}^4\text{Na}^+ \leftrightarrow \text{X}^5(\text{Ba, Sr, Pb})^{2+} \text{X}^4\Box$ .

(3) Another heterovalent exchange,  $\text{X}^{2a}\text{Na}^+ \text{X}^6\text{Na}^+ \leftrightarrow \text{X}^{2a}\Box^{\text{X6b,c}}(\text{Fe, Ca, Sr})^{2+}$ , explains the presence of M-type cations exceeding 13 apfu in all the studied samples but Branchville.

(4) The presence of a total number of M and X cations exceeding 20 argues for a substitution of the type  $\text{Na} \leftrightarrow \text{H}$ , which is actually observed at the X7 and H3x sites, respectively, in Branchville dickinsonite.

### THE NEW SITE NOMENCLATURE

Most of the compositional observed variations are controlled by two heterovalent exchanges, one involving the X5 and X4

sites, the other the X6 and X2a sites. To emphasize this control and facilitate species identification, we introduce a new site nomenclature that singles out the two relevant pairs of sites (as A1-A2 and B1-B2)—and takes into account that Cc is the actual space group. The relations between the site nomenclature used in the Cc (Cámara et al. 2006) and in the C2/c (Moore et al. 1981) space group are given in Table 2, where a and b indicate couples of sites that are no longer equivalent, P1x is now the new P site deriving from Cc symmetry, and the X sites have been renamed and rationalized in light of the active crystal-chemical exchanges.

As a result, the fundamental structural formula for the arrojadite group is



and the main substitutions accounting for the compositional variations of the group are:

- [1]  $\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+} \leftrightarrow \text{Mg} \leftrightarrow \text{Li} \leftrightarrow \text{Zn}$  at the M sites;
- [2]  $2(\text{K,Na})^+ \leftrightarrow (\text{Ba, Sr, Pb})^{2+} + \Box$  at the A1 and A2 sites;
- [3]  $2\text{Na}^+ \leftrightarrow ({}^{\text{M}}\text{Fe}^*, \text{Ca, Sr})^{2+} + \Box$  at the B1 and B2 sites, where  ${}^{\text{M}}\text{Fe}^*$  is the amount of small divalent cations occurring at the X-sites, i.e., M-type cations in excess of 13;
- [4]  $\text{OH} \leftrightarrow \text{F}$  at the W sites;
- [5]  $\text{Al} \leftrightarrow (\text{Fe}^{3+}, \text{Sc, Ti}^{4+})$  at the Al site (extremely rare);
- [6]  $\text{H} \leftrightarrow (\text{Na, } {}^{\text{M}}\text{Fe}^*)$  at the H3x and Na3 sites (only in the sample from Branchville);
- [7] the incorporation of Li at the M sites is balanced by different substitutions, involving either divalent (vs. monovalent) or monovalent (vs. vacancy) cations at the X-sites, mostly B1.

On this basis, the following ideal charge arrangements are to be considered for classification purposes:

- (1)  $\text{A}_2^{\frac{1}{2}} \text{B}_2^{\frac{1}{2}} \text{Ca} \text{Na}_2 (\text{Fe,Mn})_{13} \text{Al} (\text{PO}_4)_{11} (\text{PO}_3\text{OH}) \text{W}_2$
- (2)  $\text{A}_2^{\frac{1}{2}} \text{B}^{2+} \text{Ca} \text{Na}_2 (\text{Fe,Mn})_{13} \text{Al} (\text{PO}_4)_{11} (\text{PO}_3\text{OH}) \text{W}_2$
- (3)  $\text{A}^{2+} \text{B}_2^{\frac{1}{2}} \text{Ca} \text{Na}_2 (\text{Fe,Mn})_{13} \text{Al} (\text{PO}_4)_{11} (\text{PO}_3\text{OH}) \text{W}_2$
- (4)  $\text{A}^{2+} \text{B}^{2+} \text{Ca} \text{Na}_2 (\text{Fe,Mn})_{13} \text{Al} (\text{PO}_4)_{11} (\text{PO}_3\text{OH}) \text{W}_2$
- (5)  $\text{A}_2^{\frac{1}{2}} \text{B}_2^{\frac{1}{2}} \text{Ca} \text{Na}_3 (\text{Fe,Mn})_{13} \text{Al} (\text{PO}_4)_{11} (\text{PO}_4) \text{W}_2$
- (6)  $\text{A}_2^{\frac{1}{2}} \text{B}^{2+} \text{Ca} \text{Na}_3 (\text{Fe,Mn})_{13} \text{Al} (\text{PO}_4)_{11} (\text{PO}_4) \text{W}_2$

where  $\text{A}^{2+}$  are large divalent cations with a high coordination number (8; e.g., Ba, Sr, Pb) and  $\text{B}^{2+}$  are small divalent cations with a low coordination number (4–6; e.g., Fe, Mg, Mn, Zn, i.e.,

**TABLE 2.** Correspondence of the arrojadite site nomenclatures used in the Cc (new, this study) and C2/c space group (old, in italics, Moore et al. 1981)

old (C2/c)	new* (Cc)	old	new*	old	new*
X1	Ca	M1	M1	P1	P1
X2	B2, Na2	M2	M2a, M2b	P1x	P1x
X3	Na1	M3	M3a, M3b	P2	P2a, P2b
X4	A2	M4	M4a, M4b	P3	P3a, P3b
X5	A1	M5	M5a, M5b	P4	P4a, P4b
X6	B1 (B1x, B1y)	M6	M6a, M6b	P5	P5a, P5b
X7	Na3	M7	M7a, M7b	P6	P6a, P6b
Al	Al	O25	W1, W2		
O1 to O24	maintain their name, but double (hence a, b)				

\* a and b indicate couples of sites that are no longer equivalent.

the M-type cations in excess of 13, i.e.,  ${}^M\text{Fe}^*$ ).

The total content of the non-(P,AI) cations may reach 21 apfu when the Na3 site is fully occupied (i.e., the H3x site is empty; charge arrangement 5) but generally varies between 20 apfu (charge arrangements 1 and 6) and 18 (charge arrangement 4). The number of X-type large cations (Na + K + Ca + Sr + Ba + Pb) varies between 8 (arrangement 5) and 4 (arrangement 4), and that of M-type cations between 13 and 14, thereby accounting for the ranges found in Table 1. The above formulae do not account for possible disorder of divalent ions between the B1 and Ca sites, but such disorder does not affect the overall charge arrangement anyway.

## NOMENCLATURE OF THE ARROJADITE GROUP

### Principles

If the content of each site is considered for nomenclature, the number of independent cation sites in the formula-unit has the potential to yield a wealth of mineral names in the arrojadite group. Regardless of whether or not such proliferation would be a service to Mineralogy, the mixed occupancy of most sites (by Fe, Mn, Mg, and Li in the M sites; by Ca, Na, Fe, and vacancies in several X sites) makes a unique assignment of site population impossible in most instances, even if individual site-scattering values are known through crystal-structure refinement. This reason alone is a call for simplicity, another one being the need for a practical nomenclature, i.e., one that can be applied on the basis of chemical data alone, without resorting to structure refinement. As a matter of fact, with one exception, all previous workers refrained from introducing new root-names in the arrojadite–dickinsonite group, even when they had sufficient data for creating new species (e.g., Huvelin et al. 1972; Moore et al. 1981). We remain in this spirit and propose a practical nomenclature scheme based on the two historical root-names, in which the use of a few suffixes allows one to account for the compositional variety and to recast it on the crystal-chemical basis deciphered in the present series of papers. This nomenclature scheme was approved by the IMA-CNMMN (vote 05-D) in September 2005.

The underlying principles are: (1) to offer a crystal-chemical basis for the naming of the present and forthcoming new members of the group; (2) to limit the number of prefixes (by keeping both arrojadite and dickinsonite as root-names, although they are related by a simple homovalent exchange); (3) to use a suffix to identify each of the other main substitutions, thereby reducing the number of root-names to the minimum; (4) to remain practical, considering that crystal-structure refinement is not a routine technique and that EMP analyses are the standard source of chemical data.

### Handling heterovalent substitutions

If one ignores temporarily the Na3 for H3x substitution, the crystal chemistry of the group is governed by two heterovalent substitutions ([2] and [3] above) acting independently in two pairs of coupled sites, A1-A2 and B1-B2, each of them being charge balanced by replacement of  $\text{Na}^+$  by a vacancy at the A2 and B2 sites, respectively. For nomenclature purposes, it is sufficient to consider the dominant cation of the dominant valence state at the A1 and B1 site, respectively, to fix the proper suffixes. By so

doing, the crystal chemistry of the four relevant sites of the species is completely specified. Indeed, if a divalent cation is used as the suffix for A1 (respectively B1), vacancies are necessarily dominant at A2 (resp. B2); if a monovalent cation is used as the suffix for A1 (resp. B1),  $\text{Na}^+$  is necessarily the dominant cation at A2 (resp. B2). As a result, only two suffixes are sufficient for a full characterization, and the end-member formula that can be derived from the suffixed name is automatically charge-balanced (as in the above list of possible charge arrangements, and in Table 3).

On consideration of these advantages, we implement the 50% (or dominant-ion) nomenclature rule (e.g., Nickel 1992) for the arrojadite group as follows: “in a relevant site, the *dominant cation of the dominant valence state* is considered for nomenclature.” Note that, in case of multiple occupancy of a site involved in heterovalent exchange, the dominant cation of the dominant valence state may not be the site predominant cation. For instance, one may have 0.35 K, 0.25 Na, and 0.4 Ba in A1, and the relevant suffix will be K (and not Ba), signifying thereby that the coupled A2 site is dominantly occupied by Na.

### Criteria for arrojadite-group nomenclature

**Root name.** The partitioning of Fe, Mn, Mg, Li (and Zn) both among the 13 independent M sites and among the M and X sites is ignored for practical reasons [the possible presence of two light elements (Li and Mg) and two heavier ones (Mn and Fe) often makes a unique site assignment illusory, even in the presence of a structure refinement]; only the dominant cation among them taken as a bulk is considered (substitution [1] above) by the choice of the root-name: (1) Fe dominant, *arrojadite* series; (2) Mn dominant, *dickinsonite* series; (3) Mg dominant (if any), a new root name.

For the sake of consistency, and in the light of the following scheme that adopts suffixes based on the dominant heterovalent substitution and the nature of its predominant cation at the A and B sites, *the name sigismundite is abolished*.

**First suffix.** The dominance ( $>0.5$  pfu) of monovalent or divalent cations at the A1 site (heterovalent substitution [2] with the relevant vacancy in A2) is represented by a first suffix identifying the *dominant species of the dominant valence state*. For practical use (because we cannot distinguish from chemical analysis whether or not  $\text{A}^{2+}$  disorders between the Ca and A1 site), the default composition  $\text{X}^{2+} = \text{Ca} + \text{Sr} + \text{Pb} + \text{Ba} = 1.5$  apfu is used as a chemical divide for dominance of divalent cations at the A sites. In other words, before divalent ions are assigned to A1, the Ca site is first filled with Ca and  $\text{A}^{2+}$  ions of *increasing radius* [as available structure refinements for (Ba, Sr)-rich members (Demartin et al. 1996; Part I) indicate some Sr occupancy rather than Ba or Pb at the Ca site, in line with ionic size considerations].

**Second suffix.** A further distinction is based on the occupancy of the B sites, taking  ${}^M\text{Fe}^* = \text{Fe}^{2+} + \text{Mn}^{2+} + \text{Mg} + \text{Zn} + \text{Li} - 13 = \Sigma\text{M}^{2+} + \text{Li} - 13$  at the X sites as a measure of it.

If  ${}^M\text{Fe}^* \leq 0.5$  pfu, “Na” is used as second suffix to indicate that the B1 site is dominantly occupied by Na, and the B2 site as well.

If  ${}^M\text{Fe}^* > 0.5$  pfu, “Fe” or “Mn” (the dominant M-type cation) is used as second suffix to indicate that B1 is dominantly occupied by a divalent cation, with charge compensation by (dominant)

vacancies at the B2 site.

**Third suffix.** The general arrojadite formula has 3 (OH,F) atoms pfu. The possible dominant deficiency in H3x and related occupancy at the Na3 site are noted by addition of one more suffix indicating the dominant Na3 species. From the present experience, this suffix can be only Na. The simplest measure of Na3 occupancy is the difference between 7 (the number of A, B, Na1, Na2, and Ca sites) and the total number of cations occupying the X sites and of vacancies in A and B sites pfu,  $X_T = X^{2+} + X^+ + {}^M\text{Fe}^* + {}^A\Box + {}^B\Box$ . This value can be estimated from chemical data (the empirical formula) because, to a first approximation,  ${}^A\Box = X^{2+} - 1$  (substitution [2]) and  ${}^B\Box = {}^M\text{Fe}^* - \text{Li}$  (substitutions [3], [7]); therefore  $X_T = 2 {}^M\text{Fe}^* + 2 X^{2+} + X^+ - \text{Li} - 1$ . If  $X_T \geq 7.5$ , a third suffix is applied. However, this calculation ignores the effect of minor substitutions like Ti, and Si, or an excess of Al over 1 pfu. A simple, rigorous but only sufficient condition for dominant Na3 occupancy and for the use of the third suffix is that the sum of M-type ( $\Sigma\text{M}$ ) and X-type ( $\Sigma\text{X}$ ) cations is  $> 20.5$  apfu.

**First prefix.** The homovalent substitution  $\text{OH} \leftrightarrow \text{F}$  at the W sites is accounted for by the use of the prefix “fluor” when F is dominant over OH (i.e.,  $F > 1$  apfu).

**Second prefix.** The prefix “ferri” should apply when  $\text{Fe}^{3+}$  is dominant over Al at the Al site, as in the synthetic arrojadite phase of Yakubovich et al. (1986), or as suggested by analysis no. 3 of Robinson et al. (1992).

The suffixes are written within parentheses as extended Levinson modifiers. Indeed, they act exactly as those for rare-earth elements (REE) in a structure like epidote, for instance, for which the use of a REE suffix specifies that trivalent (REE) cations are dominant in the Ca2 site, and the element symbol specifies which cation is predominant (but may not be the site-

dominant cation, e.g., the use of “-(Ce)” with 0.30 Ce, 0.25 La, and 0.45 Ca).

### Practical steps: Formula recalculation

A high-quality analysis is mandatory for a proper crystal-chemical description of the arrojadite group and correct name assignment. Indeed, given the high charge of P and the many P atoms in the formula unit of arrojadite, a mere uncertainty of  $< 1\%$  in P stoichiometry (e.g., 0.1 P pfu) converts into 0.5 charge, i.e., 50% of a complete heterovalent substitution on any site — which makes the identification of vacancies and subtle substitutions a challenge. As a matter of fact, even in the presence of accurate and complete analyses when normalizing to 47 O and 3 (OH, F), small deviations from the ideal P content ( $\pm 0.05$  apfu) affect X cation contents in a way that may prevent a correct classification. The same is true in the case of normalization to 12 P pfu (and H by charge balance), which amplifies the effect of small P errors on the sums of X and M cations and therefore on the number of vacancies.

In spite of this inherent shortcoming, a first-step calculation with the latter normalization (12 P basis and H calculated to charge-balance the 50 O atoms corrected for F— and for  $\text{Fe}^{3+}$  replacing Al) proves quite useful. The resulting H + F pfu value has to be compared to the ideal value of 3. If Li was analyzed, H + F should be equal to 3, and any significantly lower value should be indicative of H3x deficiency, i.e., Na3 population. As shown below, this issue can be tested independently. In case no Li analysis is available, the calculated H' number is actually H + Li. Any value of H' + F significantly higher than 3 is indicative of the presence of Li, and values lower than 3 again suggest H3x deficit. Considering that all errors are cumulative in this final charge-balance exercise, the point is: what is meant by *significantly* higher or lower than 3? As

**TABLE 3.** Nomenclature (of the cation sites), charge arrangement, known compositions (given as end-member), and relevant names for arrojadite-group minerals

Ch. Arr.	A1	A2	B1	B1b,c	B2	Ca	Na1	Na2	Na3	Al	M	P	W	Name	Former name
1.	K	Na	Na		Na	Ca	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	Arrojadite-(KNa)	Arrojadite
2.	K	Na		<u>Fe</u>	$\Box$	<u>Ca</u>	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	Arrojadite-(KFe)	Arrojadite
2.	Na	Na		<u>Fe</u>	$\Box$	<u>Ca</u>	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	“Arrojadite-(NaFe)”	Arrojadite
3.	Ba	$\Box$	Na		Na	Ca	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	“Arrojadite-(BaNa)”	
4.	Ba	$\Box$		<u>Fe</u>	$\Box$	<u>Ca</u>	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	Arrojadite-(BaFe)	Baryan arrojadite, sigismundite
4.	Sr	$\Box$		<u>Fe</u>	$\Box$	<u>Ca</u>	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	Arrojadite-(SrFe)	
4.	Pb	$\Box$		<u>Fe</u>	$\Box$	<u>Ca</u>	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	Arrojadite-(PbFe)	Arrojadite
6.	K	Na		<u>Mn</u>	$\Box$	<u>Ca</u>	Na	Na	<u>Na</u>	Al	$\text{Mn}_{13}$	$(\text{PO}_4)_{11} \text{PO}_4$	$(\text{OH})_2$	Dickinsonite-(KMnNa)	Dickinsonite
5.	K	Na	Na		Na	Ca	Na	Na	Na	Al	$\text{Mn}_{13}$	$(\text{PO}_4)_{11} \text{PO}_4$	$(\text{OH})_2$	“Dickinsonite-(KNaNa)”	Dickinsonite
1.	K	Na	Na		Na	Ca	Na	Na	$\Box$	Al	$\text{Mn}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	“Dickinsonite-(KNa)”	Dickinsonite
1.	Na	Na	Na		Na	Ca	Na	Na	$\Box$	Al	$\text{Mn}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	“Dickinsonite-(NaNa)”	Dickinsonite
1.	K	Na	Na		Na	Ca	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$\text{F}_2$	“Fluorarrojadite-(KNa)”	unnamed arrojadite variety
3.	Ba	$\Box$	Na		Na	Ca	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$\text{F}_2$	Fluorarrojadite-(BaNa)	Arrojadite baryfère
4.	Ba	$\Box$		<u>Fe</u>	$\Box$	<u>Ca</u>	Na	Na	$\Box$	Al	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$\text{F}_2$	Fluorarrojadite-(BaFe)	Arrojadite baryfère
3.	Ba	$\Box$	Na		Na	Ca	Na	Na	$\Box$	$\text{Fe}^{3+}$	$\text{Fe}_{13}$	$(\text{PO}_4)_{11} \text{PO}_3\text{OH}$	$(\text{OH})_2$	“Ferri-arrojadite-(BaNa)”	unnamed arrojadite variety

Notes: Underlining indicates possible cation disorder over these sites. Names between quotation marks still need further characterization and IMA-CNMMN approval.

a guide, in our experience Li contents range between 0 and 1 pfu, H3x between 0.4 and 1 pfu, and series of analyses done in succession on a homogeneous crystal yield mean calculated H values with standard deviations of 0.2 to 0.3. Clearly, the indication obtainable from the H or H' value is a rough one, just sufficient to suggest the Branchville and Nickel Plate Mine material as candidates for H3x deficiency, and Sidi-bou-Kricha, Sapucaia, and Victory Mine as potential Li-bearers, when looking only at our batch of EMP analyses.

We suggest the following alternative procedure (used in Table 1) to recalculate chemical analyses for classification purposes, especially with analyses from different sources.

In the presence of Li analyses: (1) Normalize on 47 O and 3 (OH, F) pfu. Modify the  $P_2O_5$  so as to obtain exactly 12 P and 3 (OH,F) pfu. Calculate the  $Fe^{3+}$  content by filling the Al site if needed ( $Fe^{3+} = 1 - Al - Sc - Ti^{4+}$ ). (2) If the sum of M-type ( $\Sigma M$ ) and X-type ( $\Sigma X$ ) cations is  $>20$  apfu (a rigorous sufficient condition for partial occupancy of the Na3 site), lower the  $H_2O$  content so that  $(OH, F) = 2 + (21 - \Sigma M - \Sigma X)$ . [Note that  $X_T > 7$  is a more generally valid condition of Na3 site occupancy, allowing calculation of  $(OH, F) = 3 - (X_T - 7)$ , i.e., using the above expression of  $X_T$ ,  $(OH, F) = 37 - 2 \Sigma M^{2+} - Li - 2 X^{2+} - X^+$ . However, as the expression of  $X_T$  is slightly approximate, so is the latter of  $(OH, F)$ , which yet keeps an indicative value.] (3) Recycle the procedure to convergence.

In the absence of any occupancy at the Na3 site, i.e., under the assumptions of 12 P, 47 O, 3 (OH,F) and 1 (Al,  $Fe^{3+}$ , Sc) pfu, the electroneutrality of the formula requires that  $Li = 34 - 2 \Sigma M^{2+} - 2 X^{2+} - X^+$ . This relation always must be verified (within the uncertainties introduced by Si, Ti, Al excess, etc.) and any serious departure of the calculated Li value from the analytical value may therefore be used to identify samples with Na3 occupancy. The results of this calculation ( $Li_{calc}$ ) are shown in Table 1, identifying the Nickel Plate Mine sample as a further candidate for partial Na3 occupancy. (Incidentally, the same calculation done without the above P correction leads to  $Li_{calc}$  varying erratically between  $-0.7$  and  $+0.5$  apfu, showing how much the 0.5 charge uncertainty introduced by a typical 0.1 P pfu uncertainty does matter.)

The presence of the Na3-type substitution can be detected independently by structure refinement and, more straightforwardly, by the plot reported in Figure 1, which compares the  $(Na + K)$  content in the unit formula with the  $\beta$  angle of the unit cell, a parameter that can be simply and reliably obtained by both single-crystal and powder diffraction. The samples with a partially occupied Na3 site (open squares) significantly deviate from the main positive trend.

#### APPLICATION AND DISCUSSION

After formula recalculation as indicated above, application of this nomenclature scheme and criteria to our analyses and those from the literature (e.g., Table 1, bottom rows) creates no problem in accounting for the known or anticipated compositional ranges. The resulting combination of root-names, suffixes, and prefixes is shown together with the relevant end-member formulae in Table 3. It confirms that the monovalent ion in A1 is overwhelmingly K, that compositions are known with Sr, Ba, or Pb as the dominant divalent ion in A1, and that dominant Na3 occupancy is restricted to some dickinsonite crystals from Branchville. The fact that all the anticipated charge arrangements (1 to 6) are encountered is evidence that the heterovalent substitution at the B sites proceeds

independently from those at the A and the Na3 sites. There are at least two instances of fluorine-dominant arrojadite: the material from Sidi-bou-Kricha, for which wet-chemical (Huvelin et al. 1972) as well as EMP analyses indicate  $F > 1$  pfu, and one analysis of Yukon Territory arrojadite by Robinson et al. (1992, analysis no. 6). The Branchville dickinsonite and our Rapid Creek Yukon sample are pure OH members. Analysis no. 3 by Robinson et al. (1992) of the Yukon Territory material would be the sole natural example of a ferri-arrojadite.

#### Extension and limitations

A subtle effect of filling the Ca site before assigning  $A^{2+}$  cations to A1 (see First suffix) is revealed by the wet-chemical analysis of Sidi-bou-Kricha barian fluorarrojadite (Table 1; Huvelin et al. 1972). The anomalously low Ca content implies that much Ba is assigned to the Ca site and, as a result, monovalent cations become arithmetically dominant at A1 (therefore the first suffix Na in Table 1, given the low K content) despite the high Ba contents of the analysis. As a matter of fact, our EMP analyses of this material show higher Ca and the same total Ba content, which leads this time to Ba dominance in A1, hence to "fluorarrojadite-(BaNa)."

Another consequence of the necessary chemical divide to specify dominance in A1 ( $X^{2+} = Ca + A^{2+} = 1.5$  apfu) is that the filling of the Ca site is completed by divalent cations whenever possible, whereas the presence of minor Na is compatible with site-scattering data. In other words, the amount of  $A^{2+}$  ions in A1 may be slightly underestimated by the criteria used for nomenclature.

The dominant occupancy of the Ca site by other divalent cations is not explicitly envisaged in the present nomenclature scheme. However, if not spurious, the low-Ca wet-chemical content of the Sidi-bou-Kricha sample (Huvelin et al. 1972) would require consideration of Ba as dominant in the Ca site; Sr also may be found some day as the dominant ion in this site, for instance in a phase with the end-member formula  $A^1Sr^{A2}B^1Fe^{B2}C^aSrNa_2Fe_{13}Al(PO_4)_{11}PO_3OH(OH)_2$ , i.e., a strontian analogue of arrojadite-(SrFe), which is actually part of the solid solution in Horrsjöberg sample (Table 1). The nomenclature scheme proposed here is flexible enough to handle such homovalent substitutions at the Ca site, conceivably in the same way as for the Al site, i.e., by an appropriate prefix like bario- or strontio-.

A more general aspect of this nomenclature is that it deliberately

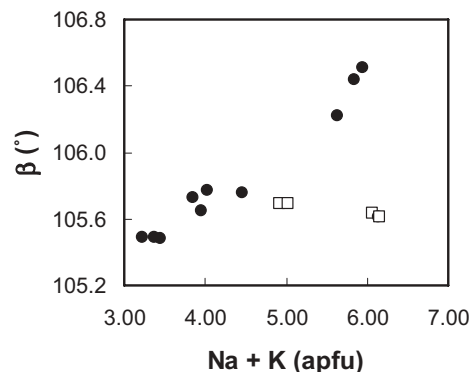


FIGURE 1. Monoclinic  $\beta$  angle as a function of the  $(Na + K)$  content for all the arrojadite samples of this study. Dots indicate samples with complete Na3 vacancy; open squares indicate samples with partial Na3 occupancy (Nickel Plate Mine and Branchville).



ignores possible disorder of  $B^{2+}$  ions between the B1 and Ca sites, and to some extent Na3 as well, whereas such disorder is suggested by the most accurate site-scattering and bond-length data (Horrjöberg, Part I, in preparation). However, as it does not affect the overall charge balance (nor the local one, except possibly around Na3) and can be resolved only by X-ray diffraction in favorable cases, such disorder is beyond the scope of a nomenclature that must be practicable on the basis of unit-cell and chemical data.

### New members

In terms of chemistry of the samples investigated or re-investigated here, only the existence of a Sr-dominant arrojadite variety (found in Horrjöberg and later in Hagendorf) is new to the mineralogical community. However, the recognition of four main independent substitution types (and two minor ones) in this mineral group leads to several combinations of root-name, suffixes, and prefixes, each combination having species status and requiring approval of the IMA-CNMMN. Among the combinations listed in Tables 1 and 3, several correspond to material from classic localities for which a complete description already exists (Branchville, Nickel Plate Mine, Sidi-bou-Kricha, Spluga). For some others, no or incomplete descriptions existed, but they could be implemented in this study (Rapid Creek, Horrjöberg, Sapucaia) also allowing formal approval. Besides, some materials for which published analyses suggest new members of the group still need to be further characterized. In the following, we examine these various cases and the status of each of the characterized members in terms of type locality and type material. The formal descriptions of the new species are compiled in the Appendix, to the extent that they are not already given in Part I, Appendix (Cámara et al. 2006).

### Status, type materials, and localities of the old and new members

**Arrojadite-(KFe).** Material from the arrojadite type-locality Serra Branca, Paraíba, Brazil (Guimaraes 1942) was restudied (optics, X-ray) on U.S. National Museum sample no. 96111 by Lindberg (1950), who confirmed its similarity to the Nickel Plate Mine material [but several Serra Branca samples in museum collections turned out to be triplite or an alteration mixture (Lindberg 1950, our study of ENSMP no. 38427)]. In the absence of a more reliable analysis than the original one, this type material cannot be specified further than arrojadite-(K), even if the pegmatitic occurrence makes an arrojadite-(KFe) composition likely. Given these uncertainties, the Nickel Plate Mine material described but not named by Headden (1891) and reinvestigated by Krutik et al. (1979), Moore and Ito (1979), Merlino et al. (1981), and Moore et al. (1981) is considered as a co-type. Our investigation of ENSMP sample no. 38431 from the same locality leads to the same conclusion. According to the proposed nomenclature, it is renamed arrojadite-(KFe) and becomes type-material for it (vote 05-D). Details on the *Cc* structure will be given in a future contribution.

**Arrojadite-(KNa).** Given the chemical uncertainty on the Serra Branca material, and the stoichiometric end-member composition of the newly investigated sample from Rapid Creek, Yukon Territory (ENSMP no. 41081, analysis in Table 1), the latter has been recognized by IMA-CNMMN as the holotype of arrojadite-(KNa) (vote 2005-047). Its mineralogical description is given in Part I. The samples from Blow River, Yukon Territory, or Victory Mine,

South Dakota, could have been used also as type material on the basis of their composition (Table 1); however, for the latter the crystal quality is much lower and apatite is intimately intergrown. Details on the structure and crystal-chemistry of these latter two samples will be given in the future.

**Arrojadite-(BaFe) and "arrojadite-(BaNa)."** The large unique holotype crystal of sigismundite from Spluga, Italy, is arrojadite-(BaFe) according to the original EMP analysis of Demartin et al. (1996) made on a petrographic thin section cut through the crystal (Table 1)—if one assumes that F (detected, non analyzed) is not dominant. The small fragment of the crystal rim we obtained from P. Gentile and F. Pezzotta is indeed OH-dominant, but is "arrojadite-(BaNa)" according to our analysis, which shows higher Na and lower Fe (Table 1, Spluga). Unless one can show that the original analysis was in error, sigismundite is renamed arrojadite-(BaFe) according to the new nomenclature, and the formal introduction of "arrojadite-(BaNa)" as a new species awaits further work. Other occurrences of arrojadite-(BaFe) are Chandler's Mills, Newport, New Hampshire, and Buranga, Rwanda (von Knorring 1969). The latter is very close to "dickinsonite-(BaMn)" by its  $Fe^{2+}/Mn$  ratio (Table 1).

**"Fluorarrojadite-(BaFe)" and fluorarrojadite-(BaNa).** The material from Sidi-bou-Kricha, Morocco (this work, Table 1) has dominant Ba and F. It is a perfect type material, completely described by Huvelin et al. (1972) and now preserved at Museum d' Histoire Naturelle De Toulouse (F. Fontan, personal communication 2006, who separated the material analyzed by Huvelin et al. 1972 and supplied us with a chip of it). The range of compositions obtained in this sample straddles the limit between "fluorarrojadite-(BaNa)" and fluorarrojadite-(BaFe), showing that the single arrojadite phase present is, depending mostly on the Li contents of the fragment considered, either "fluorarrojadite-(BaNa)" or fluorarrojadite-(BaFe). XRD data were obtained on single crystals of fluorarrojadite-(BaFe), allowing a formal description; that of "fluorarrojadite-(BaNa)" must await a more suitable sample. The mineral description (vote 2005-058a) is given in the Appendix, and details on the structure and crystal-chemistry will be given in future work. As mentioned above, the low CaO content of the original analysis by Huvelin et al. (1972) produces an apparent dominance of Ba at the Ca site and Na at the A1 site. As all the crystals we obtained from this locality show CaO contents between 2.2 and 2.4 wt%, the formal introduction of "*fluor(bario?)arrojadite-(NaFe)*" should await new findings.

**"Fluorarrojadite-(KNa)."** Analysis no. 3 of Robinson et al. (1992) on Yukon Territory material provides an example of "fluorarrojadite-(KNa)," which still needs characterization.

**Arrojadite-(SrFe).** The sample from Horrjöberg (ENSMP no. 16926) is the holotype material for arrojadite-(SrFe) (vote 2005-032). Its complete mineral description is given in Part I.

**"Arrojadite-(SrNa)."** The zoned material from Hagendorf supplied by H. Strunz to the Mineralogische Staatssammlung, Munich (sample MSM 15696), lies at the boundary between arrojadite-(SrFe) and "arrojadite-(SrNa)." Further work is needed on this sample.

**Arrojadite-(PbFe).** The wet-chemical and EMP analyses of "arrojadite" from Sapucaia, Minas Gerais, Brazil, by Moore and Ito (1979) both indicate dominant Pb at the A1 site. According to P.B. Moore (personal communication, 2005) this material may have

been discarded after he left the University of Chicago. Material from that locality supplied by P.B. Moore to ENSMP (no. 32088) was re-investigated, and our analyses (Table 1) confirm those given by Moore and Ito (1979). This sample is holotype material for arrojadite-(PbFe) (vote 2005-056). Its mineral description is summarized in the Appendix, and details on the structure and crystal-chemistry will be given in the future.

**Dickinsonite.** The material from Branchville, Connecticut, described by Brush and Dana (1878), preserved at Yale University (no. 3090), and re-investigated by Moore et al. (1981), remains type material of the dickinsonite series. The material appears to be “*dickinsonite*-(KNa)” according to one published wet-chemical analysis (no. 11 in Moore and Ito 1979), and “*dickinsonite*-(NaNa)” according to their analysis no. 9, both with a very limited excess of M + X cations over 20 apfu. New EMP analyses and structure refinement done on sample ENSMP 4861 from that locality (Part I) yield a sum of M- and X-type cations of 20.61 apfu and a Na<sub>3</sub> occupancy of 0.68 apfu. Therefore, this sample is the holotype material of *dickinsonite*-(KMnNa) (vote 2005-048). However, analyses of other crystals of the same sample indicate unit formulae within the compositional field of “*dickinsonite*-(KMn)” and “*dickinsonite*-(KNa),” showing the presence of solid solution. For memory, Buranga arrojadite is very close to “*dickinsonite*-(BaMn).”

### Perspective

The nomenclature scheme described here, based on a minimum number of root-names, has many practical advantages in making obvious the link between closely related species and in allowing, in the absence of complete characterization, a crude classification using the root-name as series name. There are precedents, like the zeolite group (Coombs et al. 1997) or, closer to arrojadite, the jahnsite–whiteite series (Moore and Ito 1978). We believe that such suffix-based nomenclature should be more generally applied to complex mineral groups, in particular to other phosphate groups.

In any event, the present chemical survey expands the compositional space of the arrojadite group. The structural formulae and nomenclature proposed here organize this space around a few major exchange vectors (identified in Part I), so that any chemical analysis can be recast into a structural formula that is a fair representation of the actual crystal chemistry. How successful are they? A few assumptions or simplifications were needed to make this nomenclature scheme applicable in the absence of crystal-structure refinement, and the question is now whether and to what extent the crystal chemistry to be revealed by a structure refinement was faithfully represented by the structural formula. This is what will be examined in the future, based on an analysis of site-scattering and bond-length data obtained on our set of samples.

### ACKNOWLEDGMENTS

This study was made possible through the help of many curators and colleagues, who made available rare materials and literature. It is a pleasure to acknowledge the contribution of Gilla Simon and Lydie Touret, of Jean-Claude Boulliard, Pierre-Jacques Chiappero, François Fontan, André-Mathieu Fransolet, Paolo Gentile, Ruprecht Hochleitner, Federico Pezzotta, and Dmitry Pushcharovsky. Olaf Medenbach is warmly thanked for measuring the optical properties of the sample from Sapucaia. Massimo Thepolo for doing LA-ICP-MS analyses, and Oliver Beyssac for help with the raman spectrometer. We also gratefully acknowledge support and constructive suggestions from members of the IMA-CNMMN, in particular Ernst Burke, Chairman, and Giovanni Ferraris, vice-Chairman. The journal referees, André-Mathieu Fransolet and Pier Francesco Zanazzi, are thanked for their patience. Funding

from the Miur-Prin 2005 project “From minerals to materials: crystal-chemistry, microstructures, modularity, modulations” is acknowledged.

### REFERENCES CITED

- Brush, G.J. and Dana, E.S. (1878) On a new and remarkable mineral locality in Fairfield County, Connecticut; with a description of several new species occurring there. *American Journal of Science*, 16, 33–46, 114–123.
- Cámara, F., Oberti, R., Chopin, C., and Medenbach, O. (2006) The arrojadite enigma: I. A new formula and a new model for the arrojadite structure. *American Mineralogist*, 91, 1249–1259.
- Cassedanne, J.P. and Baptista, A. (1999) Famous mineral localities: the Sapucaia pegmatite, Minas Gerais, Brazil. *The Mineralogical Record*, 30, 347–360, 365–366.
- Coombs, D.S., Alberti, A., Armbruster, T., Artioli, G., Colella, C., Galli, E., Grice, J.D., Liebau, F., Mandarino, J.A., Minato, H., Nickel, E.H., Passaglia, E., Peacor, D.R., Quartieri, S., Rinaldi, R., Ross, M., Sheppard, R.A., Tillmanns, E., and Vezzalini, G. (1997) Recommended nomenclature for zeolite minerals: report of the subcommittee on zeolites of the International Mineralogical Association, Commission on new minerals and mineral names. *Canadian Mineralogist*, 35, 1571–1606.
- Demartin, F., Gramaccioli, C.M., Pilati, T., and Sciesa, E. (1996) Sigismundite, (Ba,K,Pb) Na<sub>3</sub>(Ca,Sr) (Fe,Mg,Mn)<sub>14</sub>(OH)<sub>2</sub>(PO<sub>4</sub>)<sub>12</sub>, a new Ba-rich member of the arrojadite group from Spluga valley, Italy. *Canadian Mineralogist*, 34, 827–834.
- Fisher, D.J. (1954) Arrojadite is a ferroan-dickinsonite. *American Mineralogist*, 39, 676–680.
- (1965) Dickinsonites, fillowite and alluaudites. *American Mineralogist*, 50, 1647–1669.
- Guimaraes, D. (1942) Arrojadite, um novo mineral do grupo da wagnerita. *Boletins da Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo*, 30 (Mineralogia no. 5), 1–16.
- Headen, W.P. (1891) A new phosphate from the Black Hills of South Dakota. *American Journal of Science*, 41, 415–417.
- Huvelin, P., Orliac, M., and Permingeat, F. (1971) Graftonite et sarcopside de Sidi-bou-Othmane (Jebilet, Maroc). *Notes du Service géologique du Maroc*, 31(n. 237), 277–284.
- (1972) Arrojadite baryfère de Sidi-bou-Kricha (Jebilet, Maroc) et composition chimique des arrojadites et dickinsonites. *Notes du Service géologique du Maroc*, 32(n. 241), 51–66.
- Krutik, V.M., Pushcharovskii, D.Yu., Pobedimskaya, E.A., and Belov, N.V. (1979) Crystal structure of arrojadite. *Kristallografiya*, 24, 743–750.
- Lindberg, M.L. (1950) Arrojadite, hühnerkobelite, and graftonite. *American Mineralogist*, 35, 59–76.
- Mason, B. (1941) Minerals of the Varuträsk pegmatite XXIII. some iron-manganese phosphate minerals and their alteration products, with special reference to material from Varuträsk. *Geologiska Föreningens i Stockholm Förhandlingar*, 63, 117–175.
- Merlino, S., Mellini, M., and Zanazzi, P.F. (1981) Structure of arrojadite, KNa<sub>4</sub>CaMn<sub>4</sub>Fe<sub>10</sub>Al (PO<sub>4</sub>)<sub>12</sub>(OH,F)<sub>2</sub>. *Acta Crystallographica*, B37, 1733–1736.
- Moore, P.B. and Ito, J. (1978) I. Whiteite, a new species, and a proposed nomenclature for the jahnsite-whiteite complex series. II. New data on xanthoxenite. III. Salmonsite discredited. *Mineralogical Magazine*, 42, 309–323.
- (1979) Alluaudites, wyllieites, arrojadites: crystal chemistry and nomenclature. *Mineralogical Magazine*, 43, 227–235.
- Moore, P.B., Araki, T., Merlino, S., Mellini, M., and Zanazzi, P.F. (1981) The arrojadite-dickinsonite series, KNa<sub>4</sub>Ca(Fe,Mn<sup>2+</sup>)<sub>14</sub>Al(OH)<sub>2</sub>(PO<sub>4</sub>)<sub>12</sub>: crystal structure and crystal chemistry. *American Mineralogist*, 66, 1034–1049.
- Nickel, E.H. (1992) Solid solutions in mineral nomenclature. *Canadian Mineralogist*, 30, 231–234.
- Quensel, P. (1937) Minerals of the Varuträsk pegmatite I. The lithium-manganese phosphates. *Geologiska Föreningens i Stockholm Förhandlingar*, 59, 95.
- Robinson, G.W., Van Velthuisen, J., Ansell, H.G., and Sturman, B.D. (1992) Mineralogy of the Rapid Creek and Big Fish River area, Yukon Territory. *Mineralogical Record*, 23, 1–47.
- Steele, I.M. (2002) Arrojadite: variations in space group and composition based on four new refinements. 18<sup>th</sup> IMA General Meeting, Edinburgh. Abstracts, MO2-117.
- von Knorring, O. (1969) A note on the phosphate mineralisation at the Buranga pegmatite, Rwanda. *Bulletin du Service géologique du Rwanda*, 5, 42–45.
- Yakubovich, O.V., Matviyenko, Ye.N., Simonov, M.A., and Mel'nikov, O.K. (1986) The crystalline structure of synthetic Fe<sup>3+</sup>-arrojadites with the idealized formula K<sub>2</sub>Na<sub>5</sub>Fe<sub>24</sub>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>12</sub>(OH)<sub>2</sub>. *Vestnik Moskovskogo Universiteta, Seriya Geologiya*, 1986, 36–47.

MANUSCRIPT RECEIVED DECEMBER 14, 2005

MANUSCRIPT ACCEPTED MARCH 29, 2006

MANUSCRIPT HANDLED BY PAOLA BONAZZI

### APPENDIX: FURTHER MINERAL DATA FOR THE NEW MEMBERS OF THE ARROJADITE GROUP

Specimens investigated or re-investigated in this series of papers have been recognized as the holotype material of members of the arrojadite group. As requested by the IMA procedure, we report here further information for the complete mineral description of arrojadite-(PbFe) (vote 2005-56), and fluorarrojadite-(BaFe) (vote 2005-58a). Those of arrojadite-(KNa), arrojadite-(SrFe), and dickinsonite-(KMnNa) are given in Part I, Appendix. The experimental procedures for chemical (EMP and LA-ICP-MS) analysis have been described in detail in Cámara et al. (2006).

#### Chemistry

The ideal end-member composition of arrojadite-(PbFe) is:  $A^{1}Pb A^{2}\square^{B1}Fe B^{2}\square^{Na1.2}Na_{2.2}Na_{3}\square^{Ca}Ca MFe_{13} Al (PO_{4})_{11} P^{13}(PO_{3}OH) W(OH)_{2}$ , which requires  $P_{2}O_{5} = 37.41$ ,  $Al_{2}O_{3} = 2.23$ ,  $FeO = 44.18$ ,  $CaO = 2.46$ ,  $Na_{2}O = 2.72$ ,  $PbO = 9.81$ , and  $H_{2}O = 1.19$  wt%.

The ideal end-member compositions for fluorarrojadite-(BaFe) is:  $A^{1}Ba A^{2}\square^{B1}Fe B^{2}\square^{Na1.2}Na_{2.2}Na_{3}\square^{Ca}Ca MFe_{13} Al (PO_{4})_{11} P^{13}(PO_{3}OH) W(F)_{2}$ , which requires  $P_{2}O_{5} = 38.52$ ,  $Al_{2}O_{3} = 2.30$ ,  $FeO = 45.50$ ,  $CaO = 2.54$ ,  $Na_{2}O = 2.80$ ,  $BaO = 6.94$ ,  $F = 1.72$ , and  $H_{2}O = 0.41$  wt%.

#### Occurrence and paragenesis

Arrojadite-(PbFe) occurs in the Sapucaia pegmatite, in the município of Galileia, Rio Doce basin, Minas Gerais, Brazil, which is already the type locality of six phosphates (e.g., Cassedanne and Baptista 1999). In the late 1970s, arrojadite was abundant there and occurred with walnut-sized black grains of metamict fawcittite (P.B. Moore, in litt 2005); it was first studied by Moore and Ito (1979), whose wet-chemical and EMP analyses both suggested dominant Pb at the A1 site.

Fluorarrojadite-(BaFe) occurs in a pegmatite vein near Sidi-bou-Kricha, Sidi-bou-Othmane township, Jebilet mountains, Marrakech province, Morocco, from which arrojadite was reported and characterized by Huvelin et al. (1972), along with graftonite (Huvelin et al. 1971). The arrojadite phase is rare; it occurs as centimeter-sized dark-green nodules, not unlike green apatite, in a quartz matrix. The original analysis of Huvelin et al. (1972) material was made in Toulouse, and a chip of this material was made available to us by F. Fontan.

#### Physical and optical properties

Arrojadite-(PbFe) forms clear, up to millimeter-sized anhedral (corroded) isolated crystals in a groundmass of triphylite with some chloritized biotite and albite. The color is pale honey.

Fluorarrojadite-(BaFe) forms dark yellowish-green elongated nodules in quartz, up to 10 cm in length. The dark color and poor transparency are due to staining along cleavages and cracks, whereas small clean fragments are light yellowish green and transparent.

Mohs' hardness is 4–5 for fluorarrojadite-(BaFe) (Huvelin et al. 1972).

The streak is white for arrojadite-(PbFe) and dark yellowish-green for fluorarrojadite-(BaFe), and the luster is vitreous for all the samples. Arrojadites are non-fluorescent under the electron beam. The calculated density is 3.596 g/cm<sup>3</sup> for arrojadite-(PbFe),

and 3.650 g/cm<sup>3</sup> for fluorarrojadite-(BaFe), calculated from the unit-cell parameters obtained from the structure refinement.

Arrojadite-(PbFe) is biaxial (+), with  $\eta_{\alpha} = 1.6585(5)$ ,  $\eta_{\beta} = 1.6600(5)$ ,  $\eta_{\gamma} = 1.6680(5)$  (589 nm).  $2V_{\text{meas}} = 58.2(1)^{\circ}$  (direct measurement);  $57.5(10)^{\circ}$  from spindle-stage extinction curves;  $2V_{\text{calc}} = 47^{\circ}$  (possible range 38–60°). Dispersion:  $r > v$ . Orientation:  $x = b$ . Pleochroism: none discernible.

Optical data for fluorarrojadite-(BaFe) were taken from Huvelin et al. (1972). It is biaxial (+), with  $\eta_{\alpha} = 1.668(2)$ ,  $\eta_{\beta} = 1.670(2)$ ,  $\eta_{\gamma} = 1.682(2)$  (589 nm).  $2V_{\text{meas}} = 37(2)^{\circ}$  (direct measurement);  $2V_{\text{calc}} = 44.7^{\circ}$ . Dispersion: not discernible. Orientation:  $x = b$ ;  $y \wedge c = 5(1)^{\circ}$ . Pleochroism is very weak, with  $x$  very pale greenish and  $z \approx$  very pale yellowish.

#### X-ray single-crystal refinement

All the samples are monoclinic, space group  $Cc$ , with  $Z = 4$ .

Arrojadite-(PbFe):  $a = 16.4304(9)$  Å,  $b = 9.9745(5)$  Å,  $c = 24.5869(13)$  Å,  $\beta = 105.485(2)^{\circ}$ ,  $V = 3883.2(5)$  Å<sup>3</sup>. The  $a:b:c$  ratio is 1.6472:1.2:4.650.

Fluorarrojadite-(BaFe):  $a = 16.4970(9)$  Å,  $b = 10.0176(5)$  Å,  $c = 24.6359(13)$  Å,  $\beta = 105.649(2)^{\circ}$ ,  $V = 3920.42(5)$  Å<sup>3</sup>. The  $a:b:c$  ratio is 1.6468:1:2.4593.

Single-crystal X-ray studies were carried out by data collection in the  $\theta$  range 1.7–35°, which yielded 8332 unique reflections for arrojadite-(PbFe), 8628 for fluorarrojadite-(BaFe) ( $R_{\text{int}} = 2.3$  and 2.4%, respectively), with a completeness of 99.8%. Full-matrix refinement on  $F$  yielded  $R_{\text{int}} = 4.0$  and 3.1% and  $R_{\text{3\sigma}} = 3.0$  and 2.7%, respectively).

In arrojadite-(PbFe), the A1 site is occupied dominantly by divalent cations, and Pb is predominant among them (refined s.s. = 62.7 epfu); at the B1 site,  $Fe^{2+} > 0.5$  apfu (refined s.s. = 19.2 epfu).

In fluorarrojadite-(BaFe), the A1 site is occupied dominantly by large divalent cations (Ba, Sr, Pb), with Ba predominant (0.59 apfu), hence A2 is almost vacant (refined s.s. = 2.5 epfu). F is almost ordered at the W1 site (refined s.s. = 9.0 epfu).

#### X-ray powder diffraction

Due to the common presence of alteration and inclusions, X-ray ( $CuK\alpha$  radiation) powder diffraction data were calculated for all the samples from single-crystal data; the most intense reflections are tabulated in Table A1 for recognition purposes.

#### Type material

**Arrojadite-(PbFe).** The holotype sample no. 32088 is part of the collection of the Musée de Minéralogie, Ecole des Mines de Paris. The fragment of the holotype used for crystal structure refinement and chemical analysis is also preserved in the same collection.

**Fluorarrojadite-(BaFe).** The original holotype material (Huvelin et al. 1972) is preserved at Université Paul Sabatier, Toulouse, and has been now deposited by F. Fontan at Muséum d'Histoire Naturelle de Toulouse under no. MHNT.MIN.2006.38.1.

#### Compatibility

Arrojadite-(PbFe):  $1 - (K_p/K_C) = 0.012$ , superior.

Fluorarrojadite-(BaFe):  $1 - (K_p/K_C) = 0.005$ , superior, when the optical properties reported by Huvelin et al. (1972) are used in the calculation.

**APPENDIX TABLE 1.** X-ray powder diffraction data for fluorarrojadite-(BaFe) and arrojadite-(PbFe) calculated from single-crystal data ( $l > 10$ )

<i>h k l</i>	fluorarrojadite-(BaFe)			arrojadite-(PbFe)			<i>h k l</i>	fluorarrojadite-(BaFe)			arrojadite-(PbFe)		
	$2\theta_{\text{calc}}$	$d_{\text{calc}}$	$l/l_0$	$2\theta_{\text{calc}}$	$d_{\text{calc}}$	$l/l_0$		$d_{\text{calc}}$	$l/l_0$	$2\theta_{\text{calc}}$	$d_{\text{calc}}$	$l/l_0$	
1 1 0				10.48	8.4395	18.2	<b>3</b> 1 8	<b>31.63</b>	<b>2.8285</b>	<b>30.0</b>	<b>31.73</b>	<b>2.8196</b>	<b>32.9</b>
2 0 2	15.00	5.9044	18.7	15.03	5.8954	10.3	<b>3</b> 3 0	31.68	2.8245	27.2	<b>31.81</b>	<b>2.8132</b>	<b>28.7</b>
0 2 0	17.71	5.0088	16.5	17.78	4.9872	10.5	1 3 4	31.99	2.7972	15.7	32.10	2.7881	13.9
$\bar{3}$ 1 2	18.64	4.7593	13.3	18.73	4.7387	11.6	$\bar{5}$ 1 6	32.28	2.7729	17.0	32.43	2.7609	14.6
3 1 0				19.02	4.6651	13.6	<b>4</b> 0 8	<b>32.44</b>	<b>2.7595</b>		<b>32.56</b>	<b>2.7496</b>	<b>29.1</b>
0 2 2	19.23	4.6143	25.7	19.31	4.5966	23.0	<b>3</b> 3 1	<b>32.46</b>	<b>2.7585</b>	<b>32.9</b>	32.58	2.7482	19.7
<b>1</b> 1 4	19.46	4.5603	27.1	<b>19.49</b>	<b>4.5534</b>	<b>25.1</b>	<b>6</b> 0 2	32.60	2.7463	27.3	32.74	2.7355	22.2
$\bar{2}$ 2 2				21.28	4.1751		<b>3</b> 3 4	<b>33.11</b>	<b>2.7057</b>	<b>39.0</b>	<b>33.25</b>	<b>2.6941</b>	<b>32.3</b>
$\bar{3}$ 1 4				21.32	4.1670	}22.4	<b>2</b> 2 6	<b>33.14</b>	<b>2.7031</b>	<b>68.5</b>	<b>33.20</b>	<b>2.6982</b>	<b>54.8</b>
0 2 4				23.32	3.8151	10.9	$\bar{3}$ 3 2				33.78	2.6535	10.5
$\bar{3}$ 1 6				25.89	3.4411	11.1	1 3 6	34.63	2.5904	13.7	34.75	2.5817	13.4
<b>1</b> 1 6	<b>26.21</b>	<b>3.4003</b>	<b>31.2</b>	26.24	3.3961	24.1	0 2 8	35.17	2.5517	21.3	35.24	2.5466	21.8
3 1 4	26.93	3.3106	20.5	26.97	3.3054	21.6	<b>4</b> 2 4	<b>35.29</b>	<b>2.5433</b>	<b>38.1</b>	<b>35.37</b>	<b>2.5376</b>	<b>30.4</b>
2 2 4	27.58	3.2343	13.0	27.64	3.2267	14.5	6 0 6	35.35	2.5393	27.1	35.51	2.5280	15.0
1 3 1	27.76	3.2132	27.3				0 4 0	35.86	2.5044	22.6	36.02	2.4936	18.7
<b>2</b> 0 6	<b>27.78</b>	<b>3.2108</b>	<b>47.5</b>	<b>27.81</b>	<b>3.2082</b>	<b>43.1</b>	$\bar{6}$ 2 2	37.34	2.4081	13.1			
1 3 2	27.91	3.1962	23.8	28.04	3.1826	10.7	7 1 6	41.17	2.1927	15.8	41.36	2.1830	13.2
$\bar{2}$ 2 6	28.58	3.1234		28.70	3.1108		2 2 10	46.48	1.9535	13.7			
$\bar{3}$ 1 7	28.60	3.1214	}13.1	28.68	3.1128	}10.4	4 2 8	46.56	1.9507	13.5			
<b>4</b> 2 4	<b>29.46</b>	<b>3.0319</b>		<b>29.59</b>	<b>3.0186</b>	<b>100</b>	$\bar{2}$ 0 14	52.06	1.7567	15.9			
<b>5</b> 1 4	<b>29.47</b>	<b>3.0312</b>	<b>100</b>				$\bar{2}$ 4 10	52.09	1.7559	17.0			
<b>3</b> 3 2	<b>31.49</b>	<b>2.8413</b>	<b>34.1</b>	<b>31.63</b>	<b>2.8291</b>	<b>35.0</b>	6 4 2	52.26	1.7504	13.9			

Notes: The 10 strongest reflections for each sample are in bold.