CRYSTAL CHEMISTRY AND NOMENCLATURE OF FILLOWITE-TYPE PHOSPHATES

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ABSTRACT

The crystal chemistries of five samples of minerals belonging to the fillowite group were structurally investigated: (A) fillowite from the Buranga pegmatite, Rwanda; (B) fillowite from the Kabira pegmatite, Uganda; (C) johnsomervilleite from Loch Quoich, Scotland; (D) johnsomervilleite from the Malpensata pegmatite, Italy; and (E) chladniite from the Sapucaia pegmatite, Minas Gerais, Brazil. Their crystal structures were refined in space group $R\bar{3}$ (No. 148), using single-crystal X-ray diffraction data, to R_1 values of (A) 3.79%, (B) 3.52%, (C) 4.14%, (D) 4.04%, and (E) 5.59%. Unit-cell parameters are: (A) $a = 15.122(1)$, $c = 43.258(4)$ Å; (B) $a = 15.125(1)$, $c = 43.198(3)$ Å; (C) $a = 15.036(2)$, $c = 42.972(9)$ Å; (D) $a = 15.090(2)$, $c = 43.050(9)$ Å; and (E) $a = 15.1416(6)$, $c = 43.123(2)$ Å. The asymmetric unit contains 15 cation sites with coordinations ranging from V to IX, as well as six P sites. The complex structure can be split into three types of chains running parallel to the **c** axis. These chains are composed of edge- and face-sharing polyhedra. Detailed cation distributions were determined for all five samples, and their comparison allowed us to establish the general formula $A_3BC_{11}(PO_4)_9$ for fillowite-type phosphates, where A represents the group of sites mainly occupied by Na, B the Ca sites, and C the sites containing the divalent cations Fe^{2+}, Mn, and Mg. This formula was accepted by the CNMNC, and the four valid mineral species occurring in the fillowite group are fillowite (C = Mn), johnsomervilleite (C = Fe^{2+}), chladniite (C = Mg), and galileiite (B and C = Fe^{2+}). Stornesite-(Y) is discredited, since this mineral corresponds to Y-bearing chladniite.

Keywords: phosphate minerals, fillowite group, crystal chemistry, nomenclature.

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Introduction

Fillowite, $Na_2CaMn^{2+}_7(PO_4)_6$, is a phosphate mineral described by Brush & Dana (1878) from the Branchville pegmatite, Connecticut, USA. Its extremely complex crystal structure was solved by Araki & Moore (1981) in the $R\bar{3}$ space group; the very large unit cell, with $a = 15.282(2)$ and $c = 43.507(3)$ Å, contains 756 atoms distributed over 45 non-equivalent positions. The fillowite group also includes the isostructural minerals johnsomervilleite, Na_2Ca $Fe^{2+}_7(PO_4)_6$ (Livingstone 1980); chladniite, Na_2 $CaMg_7(PO_4)_6$ (McCoy *et al.* 1994); galileiite, Na_2 $Fe^{2+}_8(PO_4)_6$ (Olsen & Steele 1997); and stornesite-(Y), $(Y,Ca)\square_2Na_6(Ca,Na)_8(Mg,Fe)_{43}(PO_4)_{36}$ (Grew *et al.* 2006). Fillowite-type phosphates occur as primary phases in granitic pegmatites (Araki & Moore 1981, Fransolet *et al.* 1998), as inclusions in stony and iron meteorites (McCoy *et al.* 1994, Olsen & Steele 1997, Floss 1999), and in high-grade metamorphic rocks (Livingstone 1980, Grew *et al.* 2006).

The complex chemistry of fillowite-type minerals was demonstrated by Fisher (1965), and the crystal chemistry of the fillowite–johnsomervilleite series was investigated in detail by Fransolet *et al.* (1998), starting from new chemical analyses obtained from phosphate samples from Central Africa. These authors considered the crystal-chemical formula $Na_5(Ca_2 Na)_{\Sigma3}M_{22}(PO_4)_{18}$ for fillowite-type minerals and emphasized the role of Ca, which can easily attain one among the 22 M cations in the formula (per 72 O). The occurrence of trivalent cations (Fe^{3+}, Al^{3+}) and vacancies at cation sites are explained by the substitution mechanisms $Na^+ + M^{2+} \rightarrow \square + M^{3+}$ and $Na^+ + Na^+ \rightarrow \square + Ca^{2+}$. Fransolet *et al.* (1998) reported a linear correlation between unit-cell parameters and Mn content.

The fillowite structure was described by Araki & Moore (1981) as a packed derivative of the aphthitalite, also known as "glaserite", structure, K_3Na $(SO_4)_2$. The asymmetric unit contains 15 cation sites with coordinations ranging from V to VIII, as well as six P sites. The complex structure can be split into three types of chains running parallel to the **c** axis. These chains are composed of edge- and face-sharing polyhedra. Only a few structure refinements are available in the literature for fillowite-type phosphates: four natural samples of chladniite (Steele 1994, Vallcorba *et al.* 2017), Mg-rich fillowite (Ma *et al.* 2005), stornesite-(Y) (Grew *et al.* 2006), and four synthetic compounds (Domanskii *et al.* 1983, Keller *et al.* 2006, Hatert *et al.* 2009, Jerbi *et al.* 2010). The presence of water molecules was detected by Keller *et al.* (2006) in the synthetic $Na_2(Na,Mn)_{14}Mn_{44}$ $(PO_4)_{36}.H_2O$ compound.

The goal of this paper is to present new structural data obtained from five samples of fillowite-type phosphates: (A) fillowite from the Buranga pegmatite, Rwanda; (B) fillowite from the Kabira pegmatite, Uganda; (C) type johnsomervilleite from Loch Quoich, Scotland; (D) johnsomervilleite from the Malpensata pegmatite, Italy; and (E) chladniite from the Sapucaia pegmatite, Minas Gerais, Brazil. These data should shed some light on the complex crystal chemistry of the fillowite group, thereby leading to a new CNMNC-approved nomenclature scheme for these phosphates.

Analytical Methods

Electron-microprobe analyses of (C) and (E) were obtained with a CAMECA SX-50 instrument located in the Institut für Mineralogie, Ruhr-Universität Bochum, Germany (analyst H.-J. Bernhardt); those for (D) were obtained using a JEOL JXA-8200 instrument located in the Department of Earth Sciences, University of Milan, Italy (analyst P. Vignola). These instruments operated in the wavelength-dispersion mode with an accelerating voltage of 15 kV and a beam current of 5 nA. The standards were graftonite from Kabira (sample KF16; Fransolet 1975) (Fe, Mn, and P), olivine (Mg), synthetic ZnO (Zn), omphacite (Na), and orthoclase (K). The formulae were calculated on the basis of 36 P atoms per formula unit (*apfu*), according to the structural data ($Z = 3$), and the FeO and Fe_2O_3 contents were then constrained to maintain charge balance (Table 1).

The X-ray structural investigations of (A) and (B) were carried out with a Stoe IPDS 4-circle diffractometer located in the University of Stuttgart, Germany; those of (C) and (E) were carried out using a Rigaku Xcalibur diffractometer located in the Laboratory of Mineralogy, University of Liège, Belgium. The sample of johnsomervilleite from Malpensata (D) was investigated using a Rigaku-Oxford Diffraction Supernova goniometer equipped with an X-ray micro-source with a Pilatus 200 K Dectris detector and installed in the Department of Geosciences, University of Padova. Experimental details concerning the instruments, data collection, and structure refinements are given in Table 2.

The crystal structures were refined with SHELXTL (Sheldrick 2008) in the $R\bar{3}$ space group, which was confirmed from systematic absences, starting from the atomic coordinates of synthetic $Na(Na,Mn)_7Mn_{22}$ $(PO_4)_{18}\cdot0.5H_2O$ (Keller *et al.* 2006). Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the *International Tables for X-Ray Crystallography* (Wilson 1992). Cation occupancies were refined to obtain better agreement

TABLE 1. CHEMICAL COMPOSITIONS OF FILLOWITE-TYPE PHOSPHATES

	1	2	3	4	5	6	7	8	9
P_2O_5 (wt.%)	41.24	39.45	40.70	40.07	44.70	45.13	43.80	42.84	44.02
Al_2O_3	-	-	-	-	-	-	-	1.44	0.02
Fe_2O_3	2.76	-	1.98	-	-	2.55	1.84	-	5.53
FeO	17.21	19.4	19.41	20.84	26.20	24.12	19.50	19.18	15.98
MnO	27.87	28.87	26.5	26.43	5.20	4.97	14.45	12.39	13.96
MgO	0.22	0.22	-	0.45	12.90	12.62	9.49	10.12	9.42
ZnO	0.38	0.37	-	0.13	-	-	-	-	-
CaO	4.44	4.18	4.80	4.64	6.20	6.31	4.19	4.86	4.88
Na_2O	5.36	5.89	5.65	5.57	4.70	4.61	6.55	5.94	5.53
K_2O	-	0.07	0.20	0.13	-	-	0.03	0.15	0.01
Li_2O	-	-	0.11	-	-	-	-	0.60	-
H_2O	-	-	0.56	-	-	-	-	0.55	-
Total	99.48	98.45	99.91	98.26	99.90	100.31	99.85	98.07	99.35

				Cation numbers					
P (apfu)	36.180	36.000	35.948	36.000	36.006	36.000	36.000	35.504	36.000
Al	-	-	-	-	-	-	-	1.662	0.024
Fe^{3+}	2.152	-	1.554	-	-	1.810	1.344	-	4.014
Fe^{2+}	14.914	17.489	16.936	18.496	20.846	19.009	15.835	15.702	12.927
Mn^{2+}	24.462	26.358	23.418	23.757	4.190	3.966	11.885	10.274	11.422
Mg	0.340	0.354	-	0.712	18.294	17.727	13.739	14.766	13.571
Zn	0.290	0.294	-	0.102	-	-	-	-	-
Ca	4.930	4.828	5.366	5.276	6.320	6.375	4.361	5.098	5.055
Na	10.770	12.310	11.430	11.461	8.670	8.418	12.327	11.274	10.363
K	-	0.096	0.226	0.176	-	-	0.033	0.188	0.012
Li	-	-	0.462	-	-	-	-	-	-

For electron-microprobe analyses, cation numbers were calculated on the basis of 36 P atoms per formula unit, and the Fe^{2+}/Fe^{3+} ratio was calculated to maintain charge balance. For wet-chemical analyses, cation numbers were calculated on the basis of 144 O atoms per formula unit. 1. Fillowite, Buranga, Rwanda. Wet chemical analysis, Fransolet *et al.* (1998). 2. Fillowite, Buranga, Rwanda. Average of 3 electron-microprobe analyses, Fransolet *et al.* (1998). 3. Fillowite, Nyakishozua, Kabira, Uganda. Wet chemical analysis, Fransolet *et al.* (1998). 4. Fillowite, Nyakishozua, Kabira, Uganda. Average of 10 electron-microprobe analyses, Fransolet *et al.* (1998). 5. Johnsomervilleite, holotype, Loch Quoich, Scotland, Livingstone (1980). 6. Johnsomervilleite, type material, Loch Quoich, Scotland. Average of 22 electron-microprobe analyses, this work. 7. Johnsomervilleite, Malpensata, Italy. Average of 6 electron-microprobe analyses, this work. 8. Johnsomervilleite, Sapucaia, Minas Gerais, Brazil, Araki & Moore (1981). 9. Chladniite, Sapucaia, Minas Gerais, Brazil. Average of 11 electron-microprobe analyses, this work.

with the chemical compositions of the samples (Table 1). The occupancies of the P and O sites were constrained to 1, and the occupancies of the *M* cation sites were refined considering Fe, Mn, Mg, Na, or vacancies at those sites. The refined occupancies were then used to calculate the refined site-scattering values, necessary to determine the final site populations (see below). The refinements were completed using anisotropic displacement parameters for all atoms; the final conventional R_1 factors are (A) 0.0379, (B) 0.0352, (C) 0.0414, (D) 0.0404, and (E) 0.0559 (Table 2).

Final positional and equivalent displacement parameters, as well as selected bond distances, are available as supplementary material[1]; average bond distances are given in Table 3.

SAMPLE SELECTION AND DESCRIPTIONS

The fillowite samples from the Buranga (A) and Kabira (B) pegmatites are identical to those described earlier by Fransolet *et al.* (1998). In these assemblages, fillowite grains form granoblastic textures with

[1] Supplementary Data are available from the Depository of Unpublished Data on the MAC website (http://mineralogicalassociation.ca/), document "Fillowite-type phosphates, CM59, 20-00043".

TABLE 2. EXPERIMENTAL DETAILS FOR THE SINGLE-CRYSTAL X-RAY DIFFRACTION STUDY OF FILLOWITE-TYPE PHOSPHATES

	Buranga, Rwanda (A)	Kabira, Uganda (B)	Loch Quoich, Scotland (C)	Malpensata, Italy (D)	Sapucaia, Brazil (E)
Crystal dimensions (mm)	0.20 × 0.12 × 0.05	0.12 × 0.10 × 0.07	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.15	0.17 × 0.15 × 0.05
a (Å)	15.122(1)	15.125(1)	15.036(2)	15.090(2)	15.1416(6)
c (Å)	43.258(4)	43.198(3)	42.972(9)	43.050(9)	43.123(2)
V (Å^3)	8566(1)	8558(1)	8414(2)	8489(2)	8562.0(6)
Space group	$R3$	$R3$	$R3$	$R3$	$R3$
Z	6	6	6	6	6
Diffractometer	Stoe IPDS	Stoe IPDS	Rigaku Xcalibur, EOS CCD detector	Rigaku Supernova, Pilatus 200K Dectris detector	Rigaku Xcalibur, EOS CCD detector
Operating conditions	40 kV, 40 mA	40 kV, 40 mA	40 kV, 40 mA	50 kV, 0.8 mA	40 kV, 40 mA
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
Scan mode	ω scan	ω scan	φ/ω scan	φ/ω scan	φ/ω scan
$2\theta_{max}$	65.74°	65.88°	85.60°	101.88°	57.90°
Range of indices	−23 ≤ h ≤ 21	−23 ≤ h ≤ 23	−26 ≤ h ≤ 28	−32 ≤ h ≤ 32	−20 ≤ h ≤ 19
	−23 ≤ k ≤ 23	−23 ≤ k ≤ 23	−28 ≤ k ≤ 23	−32 ≤ k ≤ 32	−20 ≤ k ≤ 19
	−65 ≤ l ≤ 65	−65 ≤ l ≤ 65	−77 ≤ l ≤ 72	−93 ≤ l ≤ 93	−58 ≤ l ≤ 52
Measured intensities	41,383	41,883	55,323	328,702	23,571
Unique reflections	7053	6901	12,822	20,576	4658
Independent non-zero [$I > 2\sigma(I)$] reflections	4406	5506	6850	16620	3263
Absorption correction	Semi-empirical	Semi-empirical	Analytical numeric (crystal model)	Analytical numeric (crystal model)	Analytical numeric (crystal model)
μ (mm^{-1})	5.79	5.76	4.11	4.08	3.94
Data reduction program	SHELXTL-Plus (Sheldrick 1993)	SHELXTL-Plus (Sheldrick 1993)	CrysAlisPro (Oxford Diffraction 2007)	CrysAlisPro (Oxford Diffraction 2007)	CrysAlisPro (Oxford Diffraction 2007)
l.s. refinement program	SHELXL-93 (Sheldrick 2008)	SHELXL-93 (Sheldrick 2008)	SHELXL-93 (Sheldrick 2008)	SHELXL-93 (Sheldrick 2008)	SHELXL-93 (Sheldrick 2008)
Refined parameters	377	381	377	377	377
R_1 ($F_o > 2\sigma(F_o)$)	0.0379	0.0352	0.0414	0.0404	0.0559
R_1 (all)	0.0796	0.0463	0.0972	0.0542	0.0927
wR_2 (all)	0.0801	0.0881	0.1727	0.1831	0.2146
S (goodness of fit)	0.849	0.970	0.551	0.752	0.801
Max peak and hole in the final ΔF map ($e/$Å^3)	+0.95 and −0.98	+1.48 and −1.12	+3.16 and −1.68	+7.27 and −4.66	+2.18 and −1.01

TABLE 3. AVERAGE BOND DISTANCES (Å)

	Fillowite		Johnsomervilleites		Chladniite
	Buranga (A)	Kabira (B)	Loch Quoich (C)	Malpensata (D)	Sapucaia (E)
$M(1)$–O	2.192	2.266	2.131	2.231	2.127
$M(2)$–O	2.282	2.192	2.263	2.131	2.170
$M(3)$–O	2.177	2.156	2.107	2.098	2.109
$M(4)$–O	2.671	2.094	2.477	2.072	2.445
$M(5)$–O	2.157	2.167	2.085	2.114	2.089
$M(6)$–O	2.230	2.296	2.210	2.112	2.156
$M(7)$–O	2.264	2.296	2.246	2.201	2.118
$M(8)$–O	2.182	2.178	2.144	2.157	2.160
$M(9)$–O	2.121	2.121	2.097	2.115	2.125
$M(10)$–O	2.299	2.228	2.182	2.162	2.119
$M(11)$–O	2.295	2.261	2.283	2.048	2.168
$M(12)$–O	2.552	2.589	2.535	2.589	2.553
$M(13)$–O	2.099	2.665	2.071	2.459	2.088
$M(21)$–O	2.675	2.672	2.645	2.659	2.670
$M(31)$–O	2.580	2.549	2.576	2.549	2.610

alluaudite; both minerals are of primary origin (Fig. 1a, b). Wet-chemical analyses of these samples are given in Table 1; the resulting structural formulae are (A) $(Na_{9.858}\square_{2.142})_{\Sigma 12}(Ca_{3.088}Na_{0.912})_{\Sigma 4}(Ca_{1.842}Mn_{24.462}$ $Fe^{2+}_{14.914}Fe^{3+}_{2.152}Mg_{0.340}Zn_{0.290})_{\Sigma 44}(P_{36.180}O_{144})$ and (B) $(Na_{10.704}Li_{0.462}K_{0.226}\square_{0.608})_{\Sigma 12}(Ca_{3.274}Na_{0.726})_{\Sigma 4}$ $(Ca_{2.092}Mn_{23.418}Fe^{2+}_{16.936}Fe^{3+}_{1.554})_{\Sigma 44}(P_{35.948}O_{144})$. The unit-cell parameters, calculated from the X-ray powder diffraction patterns, are (A) $a = 15.199(2)$, $c = 43.313(10)$ Å, $V = 8665(5)$ Å^3 and (B) $a = 15.197(2)$, $c = 43.305(11)$ Å, $V = 8661(5)$ Å^3 (Fransolet et al. 1998).

The johnsomervilleite sample from Loch Quoich, Scotland (type locality; C) was loaned by Brian Jackson from the Royal Scottish Museum, Edinburgh (holotype sample, registration number 1962.16.1). The sample consists of a polished thin section containing an assemblage of metamorphic phosphates, including johnsomervilleite, graftonite, wolfeite, and fluorapatite. Johnsomervilleite appears as colorless grains, intimately intergrown with graftonite and blue vivianite (Fig. 1c). The wet-chemical analysis by Livingstone (1980) gives the formula $(Na_{8.670}$ $Ca_{1.650}\square_{1.680})_{\Sigma 12}(Ca_{4.000})_{\Sigma 4}(Ca_{0.670}Mn_{4.190}Fe^{2+}_{20.846}$ $Mg_{18.294})_{\Sigma 44}(P_{36.006}O_{144})$, while the electron-microprobe analyses performed in the present work gives the composition $(Na_{8.418}Ca_{0.887}\square_{2.695})_{\Sigma 12}(Ca_{4.000})_{\Sigma 4}$ $(Ca_{1.488}Mn_{3.966}Fe^{2+}_{19.009}Mg_{17.727}Fe^{3+}_{1.810})_{\Sigma 44}$ $(P_{36}O_{144})$ (Table 1). The unit-cell parameters calculated by Livingstone (1980) are $a = 15.00$, $c = 42.75$ Å, $V = 8330$ Å^3.

The johnsomervilleite sample from the Malpensata pegmatite (D) was found in the mine dumps, near the village of Olgiasca (Colico municipality, Lecco province, Italy). Several monocrystalline masses of

dark brown johnsomervilleite, up to 5 cm in length (Fig. 1d), were found hosted by primary albite in the upper dumps of the mine, associated with a complex primary phosphate association characterized, besides graftonite and sarcopside, by alkali and Al-bearing phosphates such as wyllieite, karenwebberite, and arrojadite-(KNa) (Hatert et al. 2016, Vignola & Diella 2007, Vignola et al. 2010, 2013, Vignola 2018). Electron-microprobe analysis of johnsomervilleite (Table 1) corresponds to the formula $(Na_{11.491}K_{0.033}$ $\square_{0.476})_{\Sigma 12}(Ca_{3.164}Na_{0.836})_{\Sigma 4}(Ca_{1.197}Mn_{11.885}Fe^{2+}_{15.835}$ $Mg_{13.739}Fe^{3+}_{1.344})_{\Sigma 44}(P_{36}O_{144})$.

The chladniite sample from the Sapucaia pegmatite (E) was collected by Baijot (2016). Chladniite forms black rounded grains with a resinous luster, included in quartz and albite. A similar sample was described by Araki & Moore (1981), who obtained chemical analyses corresponding to johnsomervilleite (Table 1). The sample investigated herein shows a structural formula of $(Na_{9.367}K_{0.012}\square_{2.621})_{\Sigma 12}(Ca_{3.013}Na_{0.987})_{\Sigma 4}$ $(Ca_{2.042}Mn_{11.422}Fe^{2+}_{12.927}Mg_{13.571}Fe^{3+}_{4.014}Al_{0.024})_{\Sigma 44}$ $(P_{36}O_{144})$.

STRUCTURE REFINEMENTS OF FILLOWITE-TYPE PHOSPHATES

The crystal structures of the fillowite-group minerals are similar to the structure of fillowite described by Araki & Moore (1981). To facilitate comparison, the labels for atom sites used in this paper are, as far as possible, identical to those given by Araki & Moore (1981): $M(1)$ to $M(11)$ have the same labels, whereas the Ca, Na1, Na2, and Na3 sites of Araki & Moore (1981) are renamed $M(12)$, $M(13)$, $M(21)$, and $M(31)$,
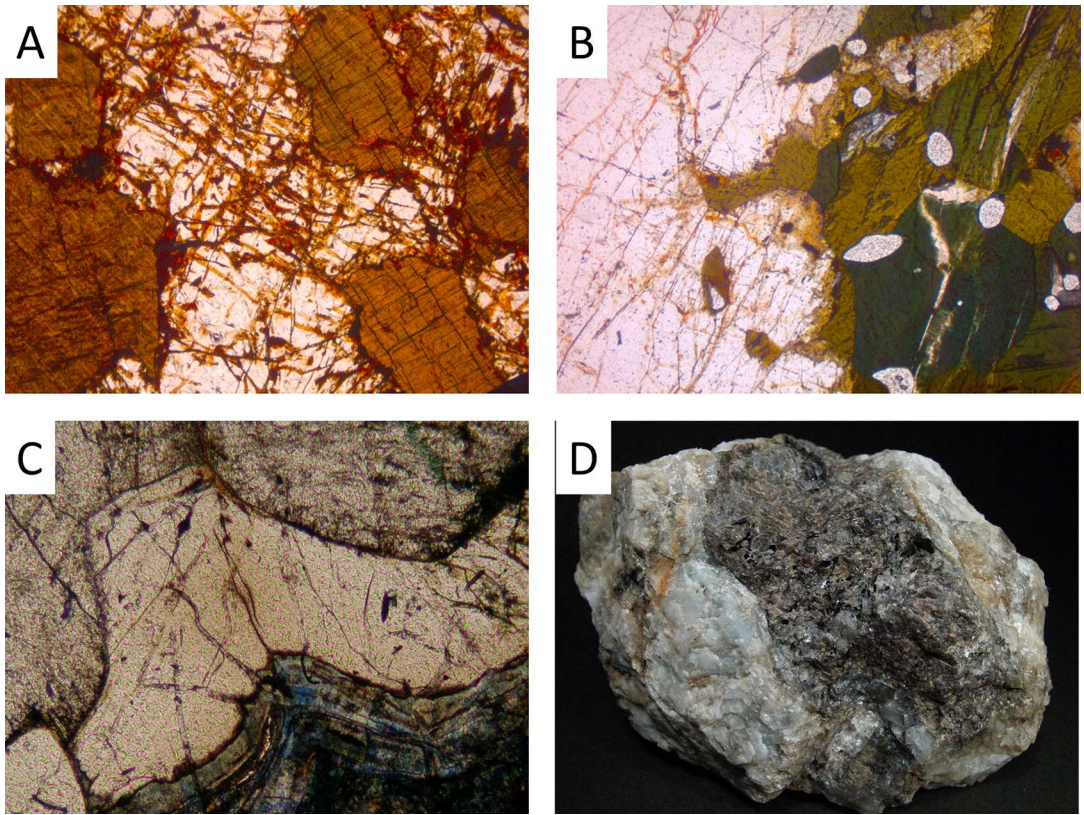
Fɪɢ. 1. (A) Photomicrograph of fillowite from the Buranga pegmatite (colorless) forming a granoblastic intergrowth with brownish grains of alluaudite-group phosphates. Plane-polarized light, length of the photograph = 2 mm. (B) Photomicrograph of fillowite from the Kabira pegmatite (colorless) intergrown with green grains of alluaudite-group phosphates containing rounded inclusions of fluorapatite. Plane-polarized light, length of the photograph = 2 mm. (C) Photomicrograph of johnsomervilleite (colorless) from the type locality, Loch Quoich, Scotland. The mineral is associated with blue vivianite and gray graftonite. Plane-polarized light, length of the photograph = 2 mm. (D) Johnsomervilleite from the Malpensata pegmatite, Italy, forming a dark mass in albite. Length of the photograph = 8 cm.

respectively. Furthermore, the crystal structures will be discussed according to the scheme of hexagonal rod-packing, which was used by Moore (1981) to describe the extraordinarily complex topology of fillowite (Fig. 2).

The hexagonal rod-packing of Moore (1981) consists of three rods parallel to the **c** axis indicated as I, II, and III. The rod coordinates in the **x-y** plane and in the asymmetric unit are as follows: rod I = (0, 0), parallel to the threefold axis; rod II = (2/3, 1/3), parallel to the 3_1 axis; and rod III = (1/9, 2/9), at the nodes of a fairly regular 6_3 net (Fig. 2b). For example, in johnsomervilleite from Loch Quoich, rod I consists of a sequence of face-sharing polyhedra and ordered vacancies: $^{VI}M(1)–\square–^{VI}M(3)–^{VI}M(13)–^{IX}M(21)–^{VI}Na(4)–^{VI}M(5)–\square–^{VI}M(2)–\square–^{VI}M(5)–^{VI}Na(4)–^{IX}M(21)–^{VI}M(13)–^{VI}M(3)–\square$ (Fig. 3a). Rod II consists of a sequence of corner- and edge-sharing polyhedra: $^{VI}M(8)–^{VIII}M(31)–^{V}M(9)–^{VII}Na(12)–^{VI}M(8)–^{VIII}M(31)–^{V}M(9)–^{VII}Na(12)–^{VI}M(8)–^{VIII}M(31)–^{V}M(9)$ (Fig. 3b). Rod III includes all PO_4 tetrahedra sharing corners with some (Fe,Mg) polyhedra; the rod is interrupted by ordered vacancies: $P(6)–^{VII}M(11)–P(4)–\square–^{VI}M(6)–P(1)–\square–P(5)–^{VI}M(7)–P(2)–^{VI}M(10)–P(3)$ (Fig. 3c).

All crystal structures of fillowite-type phosphates investigated in the present paper are similar, except some slight variations in site populations and in coordination polyhedra topologies. The assigned site populations (ASP) are given in Tables 4 (A, B) and 5 (C, D, E); these populations were calculated to obtain the best agreement of the refined site-scattering value (RSS, obtained from the refined site occupancies) with the calculated site-scattering values (CSS, calculated from the ASP) and of the bond-valence sums (BVS,
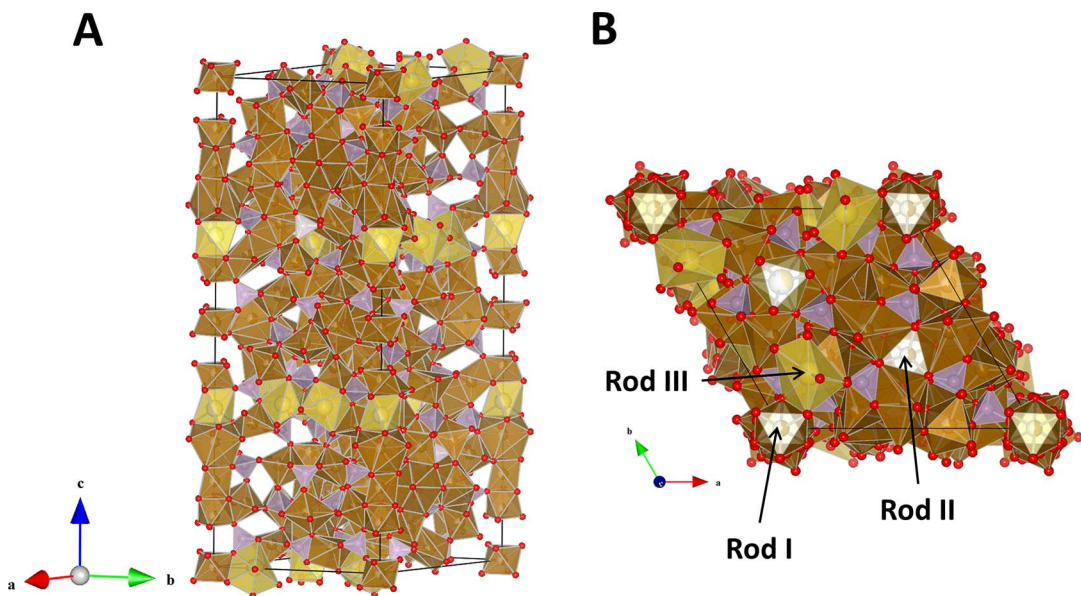
FIG. 2. The crystal structure of johnsomervilleite from Loch Quoich, projected (A) parallel or (B) perpendicular to the **c** axis. The PO$_4$ tetrahedra are purple, the (Fe,Mg)O$_x$ polyhedra are brown, and the NaO$_x$ polyhedra are yellow. The position of the three rods running along the **c** axis is shown on the (0001) projection.
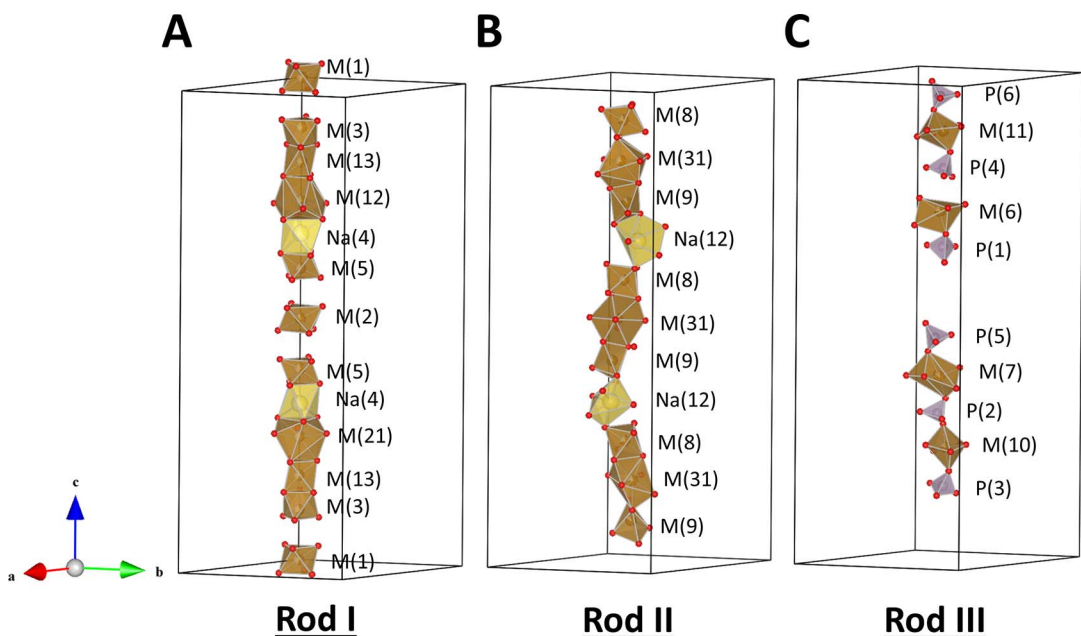

FIG. 3. The three types of rods parallel to the **c** axis in the crystal structure of johnsomervilleite from Loch Quoich. The PO$_4$ tetrahedra are purple, the (Fe,Mg)O$_x$ polyhedra are brown, and the NaO$_x$ polyhedra are yellow.

TABLE 4. ASSIGNED SITE POPULATIONS (ASP, *APFU*), REFINED SITE-SCATTERING VALUES (RSS, *EPFU*), CALCULATED SITE-SCATTERING VALUES (CSS, *EPFU*), THEORETICAL VALENCE (TV, VALENCE UNITS), BOND VALENCE SUMS (BVS, VALENCE UNITS), CHEMICAL FORMULA FROM ELECTRON-MICROPROBE (EMP), AND CHEMICAL FORMULA FROM STRUCTURE REFINEMENT (STR), FOR FILLOWITES

Site	Fillowite, Buranga, Rwanda (A)					Fillowite, Kabira, Uganda (B)				
	ASP	RSS	CSS	TV	BVS	ASP	RSS	CSS	TV	BVS
$M(1)$	1.00 Mn	23.15	25.00	2.00	2.02	0.60 Mn + 0.40 Ca	22.70	23.00	2.00	2.06
$M(2)$	0.50 Mn + 0.50 Ca	21.65	22.50	2.00	2.07	1.00 Mn	23.38	25.00	2.00	2.03
$M(3)$	0.65 Mn + 0.25 Fe^{3+} + 0.10 □	22.24	22.75	2.05	1.99	1.00 Fe^{2+}	25.38	26.00	2.00	2.09
$M(4)$	1.00 Na	10.79	11.00	1.00	1.08	0.40 Mn + 0.50 Fe^{3+} + 0.1 □	22.70	23.00	2.30	2.27
$M(5)$	0.50 Mn + 0.50 Fe^{3+}	25.45	25.50	2.50	2.33	1.00 Fe^{2+}	24.13	26.00	2.00	1.98
$M(6)$	1.00 Mn	25.00	25.00	2.00	1.99	0.40 Mn + 0.60 Fe^{2+}	25.06	25.60	2.00	2.03
$M(7)$	0.35 Mn + 0.65 Fe^{2+}	25.21	25.65	2.00	1.92	0.40 Mn + 0.60 Fe^{2+}	25.44	25.60	2.00	2.00
$M(8)$	0.55 Mn + 0.45 Fe^{2+}	25.08	25.45	2.00	1.96	0.55 Mn + 0.45 Fe^{2+}	25.12	25.45	2.00	1.99
$M(9)$	0.55 Mn + 0.45 Fe^{2+}	24.94	25.45	2.00	1.97	0.70 Mn + 0.30 Fe^{2+}	25.00	25.30	2.00	2.01
$M(10)$	0.48 Mn + 0.52 Fe^{2+}	25.29	25.52	2.00	2.04	1.00 Mn	25.00	25.00	2.00	2.02
$M(11)$	0.66 Mn + 0.34 Fe^{2+}	25.33	25.26	2.00	2.02	0.60 Mn + 0.40 Fe^{2+}	25.39	25.40	2.00	2.00
$M(12)$	1.00 Na	10.91	11.00	1.00	1.01	0.65 Ca + 0.35 Na	17.03	16.85	1.65	1.36
$M(13)$	0.60 Fe^{2+} + 0.40 Fe^{3+}	24.28	26.00	2.40	2.31	1.00 Na	11.03	11.00	1.00	1.11
$M(21)$	1.00 Na	11.31	11.00	1.00	0.88	0.10 Ca + 0.90 Na	12.08	11.90	1.10	0.94
$M(31)$	0.70 Ca + 0.30 Na	17.17	17.30	1.70	1.45	1.00 Na	11.00	11.00	1.00	1.01
EMP	$Na_{1.795}Ca_{0.822}Mn_{4.077}Fe^{2+}_{2.486}Fe^{3+}_{0.359}(PO_4)_6$					$Na_{1.905}Ca_{0.908}Mn_{3.903}Fe^{2+}_{2.823}Fe^{3+}_{0.259}(PO_4)_6$				
STR	$Na_{1.967}Ca_{0.783}Mn_{4.230}Fe^{2+}_{2.600}Fe^{3+}_{0.383}(PO_4)_6$					$Na_{1.983}Ca_{0.750}Mn_{4.050}Fe^{2+}_{3.017}Fe^{3+}_{0.167}(PO_4)_6$				

calculated from the bond lengths and the ASP, using the empirical relation of Brown & Altermatt 1985) with the theoretical valence (TV, calculated from the ASP), also taking into account the chemical compositions of the samples. As shown in Tables 4 and 5, the chemical analyses of the samples give compositions which are in good agreement with the formulae calculated from the ASP, considering the multiplicity of each crystallographic site.

Detailed site populations of the investigated samples are given in Table 6 and compared to the populations of fillowite-group minerals from the literature. This clearly shows that the cations are distributed in a very disordered way in fillowite-type phosphates: the majority of sites are occupied by at least two cations, making the determination of site populations very difficult. The cation positions $M(1)$ to $M(13)$ are generally occupied by divalent cations Mn, Fe^{2+} or Mg, except one of the two sites $M(4)$ or $M(13)$, which is dominantly occupied by Na. This group of sites corresponds to 44 M^{2+} per formula unit (*pfu*) and 2 Na *pfu*, taking into account a basis of 36 (PO$_4$) groups *pfu*, which corresponds to one-third of the unit-cell content (Table 6). Calcium is located at $M(12)$ or $M(31)$, but this position is also occupied by significant amounts of Na, with a Ca/Na ratio around 2 (Table 6). This is an example of valency-imposed double-site

occupancy (Hatert & Burke 2008), which leads to 4 Ca and 2 Na *pfu*. Significant amounts of Ca also frequently occur at $M(1)$ and $M(2)$, but the contribution of these sites of low multiplicity is negligible. Finally, Na is located at one of the two sites $M(12)$ or $M(31)$, as well as on two of the three sites $M(4)$, $M(13)$, and $M(21)$, leading to a total of 10 Na atoms *pfu*. The resulting structural formula for fillowite-group minerals is $Na_{12}Ca_4M^{2+}_{44}(PO_4)_{36}$ (Z = 3), or, more simply, $Na_3CaM^{2+}_{11}(PO_4)_9$ (Z = 12). This formula is similar to that considered by Fransolet *et al*. (1998). A summary of the cation distributions among the sites of fillowite-group phosphates is given in Table 7.

The coordination numbers of the crystallographic sites in the investigated samples are given in Table 8, where it clearly shows that the majority of sites are purely six-coordinated: $M(1)$, $M(2)$, $M(3)$, $M(5)$, and $M(8)$. $M(9)$, the smallest site of the structure, is five-coordinated, while the large Na-bearing $M(21)$ site is nine-coordinated. The two (Na,Ca)-bearing $M(12)$ and $M(31)$ sites show a coordination between seven and eight; the two $M(4)$ and $M(13)$ sites are generally six-coordinated, except when they contain high amounts of Na, inducing an increase to a coordination number of nine. Finally, the four sites $M(6)$, $M(7)$, $M(10)$, and

TABLE 5. ASSIGNED SITE POPULATIONS (ASP, *APFU*), REFINED SITE-SCATTERING VALUES (RSS, *EPFU*), CALCULATED SITE-SCATTERING VALUES (CSS, *EPFU*), THEORETICAL VALENCE (TV, VALENCE UNITS), BOND VALENCE SUMS (BVS, VALENCE UNITS), CHEMICAL FORMULA FROM ELECTRON-MICROPROBE (EMP), AND CHEMICAL FORMULA FROM STRUCTURE REFINEMENT (STR), FOR JOHNSOMERVILLEITES AND CHLADNIITE

Site	Johnsomervilleite, Loch Quoich (C)					Johnsomervilleite, Malpensata (D)					Chladniite, Sapucaia (E)				
	ASP	RSS	CSS	TV	BVS	ASP	RSS	CSS	TV	BVS	ASP	RSS	CSS	TV	BVS
M(1)	$0.84\ Mg + 0.16\ Fe^{2+}$	13.63	14.24	2.00	1.87	$1.00\ Mn$	29.35	25.00	2.00	1.82	$0.60\ Mg + 0.40\ Mn$	17.00	17.20	2.00	2.08
M(2)	$0.60\ Mn + 0.40\ Ca$	21.20	23.00	2.00	2.08	$0.40\ Mg + 0.60\ Fe^{2+}$	20.26	20.40	2.00	1.97	$0.54\ Mn + 0.46\ Fe^{2+}$	26.55	25.46	2.00	2.01
M(3)	$0.87\ Mg + 0.13\ Fe^{2+}$	13.62	13.82	2.00	2.08	$0.90\ Mg + 0.10\ Fe^{2+}$	14.40	13.40	2.00	2.14	$0.90\ Mg + 0.10\ Fe^{2+}$	14.48	13.40	2.00	2.07
M(4)	$0.45\ Na + 0.55\ \square$	4.17	4.95	0.45	0.44	$0.90\ Mg + 0.10\ Fe^{2+}$	14.35	13.40	2.00	2.19	$0.90\ Na + 0.10\ \square$	9.20	9.90	0.90	0.95
M(5)	$0.87\ Mg + 0.13\ Fe^{2+}$	13.76	13.82	2.00	2.21	$1.00\ Mg$	12.46	12.00	2.00	2.02	$0.70\ Mg + 0.30\ Fe^{3+}$	15.91	16.20	2.30	2.31
M(6)	$0.45\ Mg + 0.55\ Mn$	19.84	19.15	2.00	1.91	$0.30\ Mg + 0.70\ Mn$	21.34	21.10	2.00	1.96	$0.20\ Mg + 0.60\ Fe^{2+} + 0.20\ Ca$	21.09	22.00	2.00	1.90
M(7)	$0.20\ Mg + 0.80\ Fe^{2+}$	21.09	23.20	2.00	1.95	$0.20\ Mg + 0.80\ Fe^{2+}$	23.01	23.20	2.00	1.82	$0.40\ Mg + 0.50\ Mn + 0.10\ Fe^{2+}$	19.97	19.90	2.00	1.96
M(8)	$0.55\ Mg + 0.45\ Fe^{2+}$	18.22	18.30	2.00	1.89	$0.50\ Mg + 0.50\ Fe^{2+}$	19.48	19.00	2.00	1.83	$0.50\ Mg + 0.50\ Fe^{2+}$	19.03	19.00	2.00	1.82
M(9)	$0.32\ Mg + 0.68\ Fe^{2+}$	21.46	21.45	2.00	1.86	$0.10\ Mg + 0.65\ Fe^{2+} + 0.20\ Fe^{3+} + 0.05\ \square$	22.55	23.3	2.10	1.75	$0.20\ Mg + 0.50\ Mn + 0.30\ Fe^{2+}$	21.27	22.70	2.00	1.89
M(10)	$0.42\ Mg + 0.58\ Fe^{2+}$	20.14	20.12	2.00	1.88	$0.20\ Mg + 0.80\ Mn$	22.17	22.40	2.00	1.80	$0.20\ Mg + 0.80\ Mn$	20.54	22.40	2.00	1.96
M(11)	$0.20\ Mg + 0.80\ Fe^{2+}$	22.26	23.20	2.00	1.95	$0.30\ Mn + 0.50\ Fe^{2+} + 0.10\ Ca + 0.10\ Na$	21.97	23.6	1.90	1.92	$0.60\ Fe^{2+} + 0.10\ Fe^{3+} + 0.10\ Ca + 0.20\ Na$	21.40	22.40	1.90	1.73
M(12)	$1.00\ Na$	10.65	11.00	1.00	1.04	$0.60\ Ca + 0.40\ Na$	16.27	16.4	1.60	1.36	$1.00\ Na$	11.88	11.00	1.00	1.00
M(13)	$0.60\ Mg + 0.40\ Fe^{2+}$	14.46	17.60	2.00	2.27	$0.60\ Na + 0.40\ \square$	6.73	6.60	0.60	1.02	$0.60\ Mg + 0.40\ Fe^{3+}$	17.05	17.60	2.40	2.24
M(21)	$0.60\ Ca + 0.40\ Na$	13.73	16.40	1.60	1.25	$0.10\ Ca + 0.90\ Na$	12.27	11.90	1.10	0.96	$0.10\ Ca + 0.90\ Na$	11.66	11.90	1.10	0.96
M(31)	$0.80\ Ca + 0.20\ Na$	15.75	18.20	1.80	1.53	$1.00\ Na$	10.25	11.00	1.00	1.01	$0.15\ Fe^{3+} + 0.50\ Ca + 0.35\ \square$	14.20	13.90	1.45	0.76
EMP	$Na_{2.168}Ca_{1.580}Mn_{1.047}Fe^{2+}_{5.211}Mg_{4.574}(PO_4)_9$					$Na_{3.081}Ca_{1.091}Mn_{2.972}Fe^{2+}_{3.959}Mg_{3.435}Fe^{3+}_{0.336}(PO_4)_9$					$Na_{2.583}Ca_{1.260}Mn_{2.847}Fe^{2+}_{3.222}Mg_{3.383}Fe^{3+}_{1.001}(PO_4)_9$				
STR	$Na_{2.225}Ca_{1.601}Mn_{0.975}Fe^{2+}_{5.328}Mg_{4.598}(PO_4)_9$					$Na_{3.000}Ca_{1.100}Mn_{2.951}Fe^{2+}_{3.926}Mg_{3.450}Fe^{3+}_{0.300}(PO_4)_9$					$Na_{2.700}Ca_{1.250}Mn_{2.936}Fe^{2+}_{3.315}Mg_{3.500}Fe^{3+}_{0.725}(PO_4)_9$				

TABLE 6. CATION DISTRIBUTIONS AT THE DIFFERENT CRYSTALLOGRAPHIC SITES OF FILLOWITE-GROUP MINERALS

Site	Mult. 108 P pfu	Mult. / 3 36 P pfu	Fillowite Buranga (A)	Fillowite Kabira (B)	Johnsomervilleite Loch Quoich (C)	Johnsomervilleite Malpensata (D)	Chladniite Sapucaia (E)
$M(1)$	3	1	Mn	0.6 Mn + 0.4 Ca	0.84 Mg + 0.16 Fe^{2+}	Mn	0.6 Mg + 0.4 Mn
$M(2)$	3	1	0.5 Mn + 0.5 Ca	Mn	0.6 Mn + 0.4 Ca	0.4Mg + 0.6Fe^{2+}	0.54 Mn + 0.46 Fe^{2+}
$M(3)$	6	2	0.65 Mn + 0.25 Fe^{3+} + 0.10 □	Fe^{2+}	0.87 Mg + 0.13 Fe^{2+}	0.9 Mg + 0.1 Fe^{2+}	0.9 Mg + 0.1 Fe^{2+}
$M(4)$	6	2	**Na**	0.4 Mn + 0.5 Fe^{3+} + 0.1 □ Fe^{2+}	0.45 **Na** + **0.55** □	0.9 Mg + 0.1 Fe^{2+}	**0.9 Na** + **0.1** □
$M(5)$	6	2	0.5 Mn + 0.5 Fe^{3+}	Fe^{2+}	0.87 Mg + 0.13 Fe^{2+}	Mg	0.7 Mg + 0.3 Fe^{3+}
$M(6)$	18	6	Mn	0.4 Mn + 0.6 Fe^{2+}	0.45 Mg + 0.55 Mn	0.3 Mg + 0.7 Mn	0.2 Mg + 0.6 Fe^{2+} + 0.2 Ca
$M(7)$	18	6	0.35 Mn + 0.65 Fe^{2+}	0.4 Mn + 0.6 Fe^{2+}	0.2 Mg + 0.8 Fe^{2+}	0.2 Mg + 0.8 Fe^{2+}	0.4 Mg + 0.5 Mn + 0.1 Fe^{2+}
$M(8)$	18	6	0.55 Mn + 0.45 Fe^{2+}	0.55 Mn + 0.45 Fe^{2+}	0.55 Mg + 0.45 Fe^{2+}	0.5 Mg + 0.5 Fe^{2+}	0.5 Mg + 0.5 Fe^{2+}
$M(9)$	18	6	0.55 Mn + 0.45 Fe^{2+}	0.7 Mn + 0.3 Fe^{2+}	0.32 Mg + 0.68 Fe^{2+}	0.10 Mg + 0.65 Fe^{2+} + 0.20 Fe^{3+} + 0.05 □	0.2 Mg + 0.5 Mn + 0.3 Fe^{2+}
$M(10)$	18	6	0.48 Mn + 0.52 Fe^{2+}	Mn	0.42 Mg + 0.58 Fe^{2+}	0.2 Mg + 0.8 Mn	0.2 Mg + 0.8 Mn
$M(11)$	18	6	0.66 Mn + 0.34 Fe^{2+}	0.6 Mn + 0.4 Fe^{2+}	0.2 Mg + 0.8 Fe^{2+}	0.3 Mn + 0.5 Fe^{2+} + 0.1 Ca + 0.1 Na	0.6 Fe^{2+} + 0.1 Fe^{3+} + 0.1 Ca + 0.2 Na
$M(12)$	18	6	**Na**	0.65 Ca + 0.35 Na	**Na**	0.6 Ca + **0.4** Na	**Na**
$M(13)$	6	2	0.60 Fe^{2+} + 0.40 Fe^{3+}	**Na**	0.6 Mg + 0.4 Fe^{2+}	**0.6 Na** + **0.4** □	0.6 Mg + 0.4 Fe^{3+}
$M(21)$	6	2	**Na**	0.1 Ca + **0.9 Na**	0.6 Ca + 0.4 Na	0.1 Ca + **0.9 Na**	0.1 Ca + **0.9 Na**
$M(31)$	18	6	0.7 Ca + 0.3 **Na**	**Na**	0.8 Ca + 0.2 Na	**Na**	0.15 Fe^{3+} + 0.5 Ca + 0.35 □

Site	Mult. 108 P pfu	Mult. / 3 36 P pfu	Fillowite Araki & Moore (1981)	Chladniite Steele (1994)	Mg-fillowite Ma et al. (2005)	« Stornesite-(Y) » Grew et al. (2006)	Chladniite Vallcorba et al. (2017)
$M(1)$	3	1	0.62 Mn + 0.38 Ca	Ca	Mn	0.68 Y + 0.26 Ca + 0.06 Yb	0.60 Mn + 0.20 Fe^{2+} + 0.18 Ca + 0.02 Mg
$M(2)$	3	1	Mn	Mg	Mn	0.51 Fe^{2+} + 0.49 Mg	0.80 Mg + 0.11 Mn + 0.09 Ca
$M(3)$	6	2	Fe^{2+}	Mg	Mg	0.97 Mg + 0.03 Fe^{2+}	0.94 Mg + 0.06 Fe^{2+}
$M(4)$	6	2	Fe^{2+}	Mg	Mg	0.97 Mg + 0.03 Fe^{2+}	0.92 Mg + 0.08 Fe^{3+}
$M(5)$	6	2	Mn	Mg	Mg	Mg	0.96 Mg + 0.04 Ca
$M(6)$	18	6	Mn	Mg	Mn	0.72 Mg + 0.28 Fe^{2+}	0.50 Fe^{2+} + 0.40 Mg + 0.10 Fe^{3+}
$M(7)$	18	6	Mn	Mg	Mn	0.55 Mg + 0.45 Fe^{2+}	0.69 Mn + 0.15 Ca + 0.12 Mg + 0.04 Zn
$M(8)$	18	6	0.67 Fe^{2+} + 0.33 Mn	Mg	Fe^{2+}	0.89 Mg + 0.11 Fe^{2+}	0.56 Mg + 0.37 Mn + 0.07 Ca
$M(9)$	18	6	Mn	Mg	Mn	0.63 Mg + 0.37 Fe^{2+}	0.46 Fe^{2+} + 0.30 Mg + 0.20 Fe^{3+} + 0.04 Mn
$M(10)$	18	6	Mn	Mg	Mn	0.79 Mg + 0.21 Fe^{2+}	0.68 Mn + 0.20 Fe^{2+} + 0.12 □
$M(11)$	18	6	Mn	Mg	Mn	0.67 Mg + 0.33 Fe^{2+}	0.71 Fe^{2+} + 0.29 Mg
$M(12)$	18	6	0.65 Ca + 0.35 Na	0.69 Ca + 0.31 Na	Ca	0.58 Ca + 0.42 Na	0.65 Ca + 0.35 Na
$M(13)$	6	2	**0.91 Na** + 0.09 Ca	**0.81 Na** + 0.19 □	**Na**	0.94 □ + **0.06 Na**	0.52 □ + **0.48 Na**
$M(21)$	6	2	**0.9 Na** + 0.1 Ca	**Na**	**Na**	0.75 Ca + 0.25 Na	**0.60 Na** + **0.25 Mn** + **0.15** □
$M(31)$	18	6	**Na**	**Na**	**Na**	**Na**	**0.98 Na** + **0.02** □

Atoms located at Na-dominant sites are in bold; atoms located at Ca-dominant sites are underlined.

TABLE 7. SUMMARY OF CATION DISTRIBUTIONS AMONG THE CRYSTALLOGRAPHIC SITES
OF FILLOWITE-GROUP MINERALS

Sites	Occupancy	Total multiplicity (basis = 36 P)	Number of atoms in the formula (basis = 36 P)
$M(1)$, $M(2)$	Fe^{2+}, Mn, Mg (+ minor Ca, REE)	1 × 2 sites = 2	2 M^{2+}
$M(3)$, $M(5)$	Fe^{2+}, Mn, Mg	2 × 2 sites = 4	4 M^{2+}
$M(6)$, $M(7)$, $M(8)$, $M(9)$, $M(10)$, $M(11)$	Fe^{2+}, Mn, Mg	6 × 6 sites = 36	36 M^{2+}
$M(4)$, $M(13)$, $M(21)$	Two of these three sites are dominantly occupied by Na, while the other site is dominantly occupied by M^{2+}.	2 × 3 sites = 6	4 Na 2 M^{2+}
$M(12)$, $M(31)$	One of these two sites is dominantly occupied by Na, while the other site is dominantly occupied by (Ca, Na) with a Ca/Na ratio close to 2.	6 × 2 sites = 12	6 Na (4 Ca + 2 Na)
TOTAL			44 M^{2+} (= C sites) 12 Na (= A sites) 4 Ca (= B sites)

$M(11)$ show high versatility, with coordination numbers ranging from four to seven (Table 8).

Discussion

Nomenclature of fillowite-group minerals

Before the acceptance of the present proposal, the IMA-CNMNC mineral list contained five phosphates belonging to the fillowite group; they are reported in Table 9. Xenophyllite, $Na_4Fe_7(PO_4)_6$, is an IMA-CNMNC-accepted mineral species (2006-006) found in the Augustinovka meteorite in Ukraine, as yet unpublished. This species is referenced as belonging to the fillowite group by such websites as Mindat (www.mindat.org) and Webmineral (www.webmineral.com); however, its crystal structure is significantly different and can be compared to that of the X-phase synthesized by Hatert *et al.* (2006, 2011, 2014). Consequently, xenophyllite does not belong to the fillowite group of phosphates.

TABLE 8. COORDINATION NUMBERS FOR THE DIFFERENT CRYSTALLOGRAPHIC SITES
OF FILLOWITE-GROUP MINERALS

Site	Fillowite	Fillowite	Johnsomervilleite	Johnsomervilleite	Chladniite
	Buranga	Kabira	Loch Quoich	Malpensata	Sapucaia
$M(1)$	**[VI]**	**[VI]**	**[VI]**	**[VI]**	**[VI]**
$M(2)$	**[VI]**	**[VI]**	**[VI]**	**[VI]**	**[VI]**
$M(3)$	**[VI]**	**[VI]**	**[VI]**	**[VI]**	**[VI]**
$M(4)$	[IX]	**[VI]**	**[VI]**	**[VI]**	**[VI]**
$M(5)$	**[VI]**	**[VI]**	**[VI]**	**[VI]**	**[VI]**
$M(6)$	**[VI]**	[VII]	**[VI]**	[V]	[V]
$M(7)$	**[VI]**	[VII]	**[VI]**	**[VI]**	[V]
$M(8)$	**[VI]**	**[VI]**	**[VI]**	**[VI]**	**[VI]**
$M(9)$	[V]	[V]	[V]	[V]	[V]
$M(10)$	[VII]	**[VI]**	**[VI]**	[V]	[V]
$M(11)$	[VII]	**[VI]**	[VII]	[IV]	[V]
$M(12)$	[VII]	[VIII]	[VII]	[VIII]	[VII]
$M(13)$	**[VI]**	[IX]	**[VI]**	**[VI]**	**[VI]**
$M(21)$	[IX]	[IX]	[IX]	[IX]	[IX]
$M(31)$	[VIII]	[VII]	[VIII]	[VII]	[VIII]

Octahedral sites are in bold.

TABLE 9. NEW IDEAL FORMULAE FOR THE FILLOWITE-GROUP MINERALS

Mineral name	Old CNMNC formula	New ideal formula
Fillowite	$Na_2CaMn^{2+}_7(PO_4)_6$	$Na_3CaMn^{2+}_{11}(PO_4)_9$
Johnsomervilleite	$Na_{10}Ca_6Mg_{18}Fe^{2+}_{25}(PO_4)_{36}$	$Na_3CaFe^{2+}_{11}(PO_4)_9$
Chladniite	$Na_2CaMg_7(PO_4)_6$	$Na_3CaMg_{11}(PO_4)_9$
Galileiite	$NaFe^{2+}_4(PO_4)_3$	$Na_3Fe^{2+}Fe^{2+}_{11}(PO_4)_9$
Stornesite-(Y)	$Na_6(Ca_5Na_3)YMg_{43}(PO_4)_{36}$	Discredited

As shown in Table 9, the formulae of fillowite-group minerals, previously reported in the IMA-CNMNC mineral list, differ from mineral to mineral: the number of (PO$_4$) groups *pfu* is three for galileiite, six for fillowite and chladniite, and 36 for johnsomervilleite and stornesite-(Y). It was consequently necessary to rationalize the nomenclature by using the same general formula for all minerals of the group.

Due to the disordered cation distributions observed in all fillowite-group phosphates (Table 6) and the high complexity of this structure type, it appears unrealistic to determine these minerals on the basis of individual site occupancies. Indeed, a strict application of the dominant-constituent rule would then lead to an unnecessarily high number of new species in the group. In order to avoid such a situation, we recommend considering crystallographic sites with the same crystal-chemical behavior to be equivalent for nomenclature purposes. Such a procedure corresponds to a grouping of crystallographic sites, as described by Hatert & Burke (2008).

Applying this grouping yields three crystal-chemically distinct groups of sites in the structure: the *A* sites dominantly occupied by Na, the *B* sites dominantly occupied by Ca, and the *C* sites dominantly occupied by Mn^{2+}, Fe^{2+}, or Mg (Table 7). The general formula for fillowite-group phosphates therefore corresponds to (Z = 12): $A_3BC_{11}(PO_4)_9$.

When *A* and *B* groups of sites are dominantly occupied by Na and Ca, respectively, the species are distinguished on the basis of their *C* contents: Mn^{2+}-dominant = fillowite, Mg-dominant = chladniite, and Fe^{2+}-dominant = johnsomervilleite. In galileiite, the *A* group of sites is dominantly occupied by Na, while the *B* and *C* groups of sites are dominantly occupied by Fe^{2+}; this species is a Ca-free endmember. For hypothetical future species that would contain a dominant cation other than Na at the *A* group of sites, we recommend the addition of a chemical suffix in order to avoid the unnecessary multiplication of root-names.

This threefold categorization of the *M* sites leaves unresolved the status of stornesite-(Y), with the empirical formula $Y_{0.68}Yb_{0.06}Na_{8.69}Ca_{5.40}Sr_{0.01}$ $Mg_{30.71}Fe_{11.56}Mn_{0.18}Si_{0.02}S_{0.04}P_{36.22}O_{144}$ (Grew *et al.* 2006). In this mineral, Y and Yb are located at the *M*(1) site; these cations belong to the *C* group of sites. Redistributing the cations among the three groups of *M* sites gives the formula $^A(Na_{2.18}Ca_{0.35})_{\Sigma2.53}{}^B(Ca_{1.00})$ $^C(Mg_{7.68}Fe^{2+}_{2.89}Mn_{0.05}Y_{0.17}Yb_{0.02})_{\Sigma10.81}(PO_4)_{9.06}$; this formula corresponds to chladniite. Consequently, stornesite-(Y) is discredited since it is equivalent to a Y-bearing chladniite.

The nomenclature guidelines for the fillowite group, as well as the discreditation of stornesite-(Y), were approved by the IMA-CNMNC (Miyawaki *et al.* 2020). A summary of the new CNMNC-approved formulae is given in Table 9.

Compositional variations of fillowite-type phosphates

Starting from the general formula $A_3BC_{11}(PO_4)_9$, several substitution mechanisms can be considered, leading to the observed compositions of fillowite-type phosphates. The *C* group of sites mainly exhibits homovalent substitutions of Mn by Fe^{2+} and Mg, inducing the transition from fillowite to johnsomervilleite and chladniite, respectively. Although chladniite and fillowite can contain significant amounts of Fe^{2+},
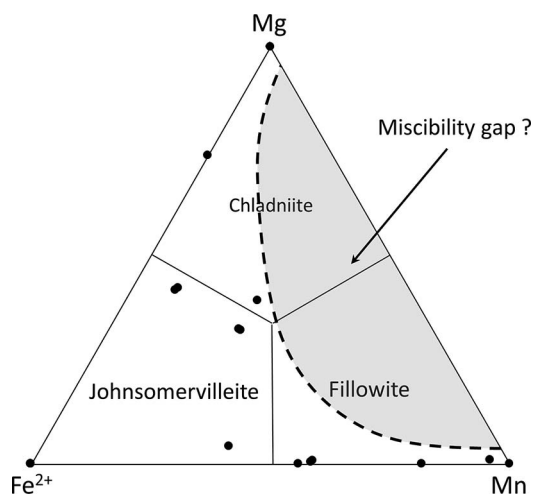

FIG. 4. Ternary Fe^{2+}–Mn–Mg diagram showing the compositions of natural fillowite-type phosphates. A possible miscibility gap between chladniite and fillowite is shaded in gray.
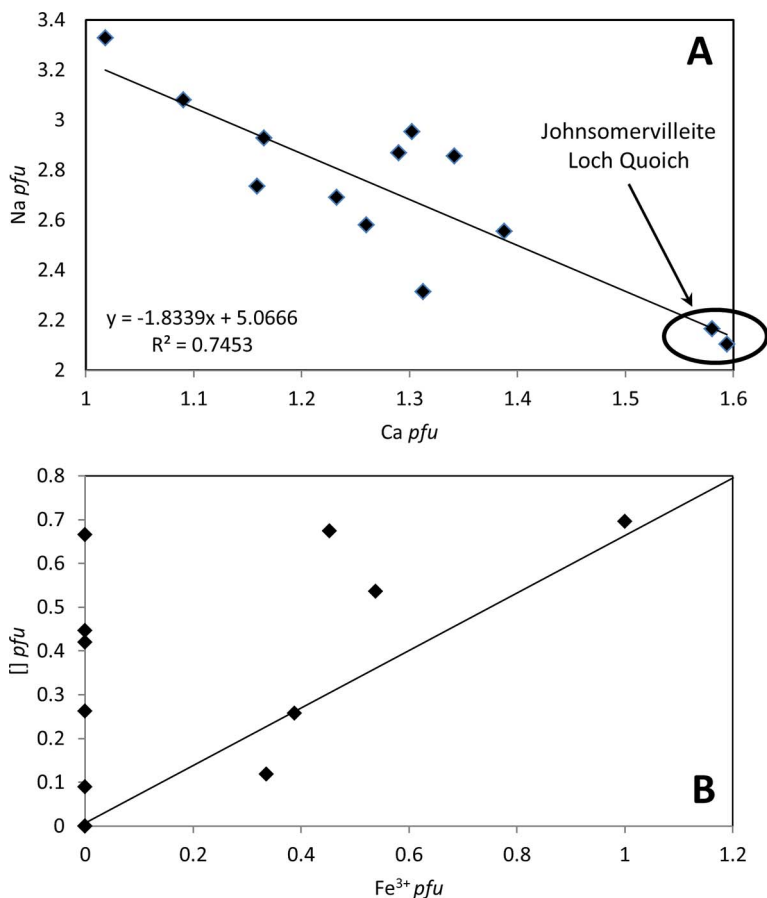
FIG. 5. Diagram showing the correlations in natural fillowite-type phosphates between (A) Na *pfu* and Ca *pfu* and (B) □ *pfu* and Fe^{3+} *pfu*.

the Mg contents of fillowite and the Mn contents of chladniite are very low (Table 1, Fig. 4), suggesting the presence of a miscibility gap. This crystal-chemical feature, previously described by Fransolet *et al.* (1998), could be due to the relatively small differences in ionic radii between the pairs of Fe^{2+} and Mn cations (ionic radii 0.780 and 0.830 Å, difference 0.050 Å, Shannon 1976) and Fe^{2+} and Mg cations (ionic radii 0.780 and 0.720 Å, difference 0.060 Å, Shannon 1976) compared to the pair of Mn and Mg cations, between which the ionic radii differ by 0.110 Å. However, the large difference does not necessarily lead to a miscibility gap in other minerals (*e.g.*, dolomite-kutnahorite, Essene 1983). Geochemical factors such as progressive enrichment of Mn and depletion of Mg and Fe in pegmatites could also contribute to the absence of chladniite–fillowite solid solutions (Fransolet *et al.* 1998); similarly, Essene (1983) noted that there may be few protoliths yielding magnesite–rhodochrosite solid solutions.

Fransolet *et al.* (1998) and Rondeux (2010) reported that the Na/Ca ratio in natural and synthetic fillowite-type phosphates generally ranges from 2 to 3, except for johnsomervilleite from Loch Quoich, which shows a significantly lower Na/Ca ratio. These variations of the Na/Ca ratio contributed to the difficulties in establishing a unique general formula for minerals of the fillowite group: the new general formula, $A_3BC_{11}(PO_4)_9$, corresponds to a Na/Ca ratio of 3, but allows for deviation from 3 because of the substitution involving vacancy, $Na^+ + Na^+ = Ca^{2+} + \square$. The formula previously proposed by Araki & Moore (1981), $Na_2Ca(Mn,Fe)_7(PO_4)_6$, is restricted to a low Na/Ca ratio of 2. Figure 5A shows an inverse correlation between Na *pfu* and Ca *pfu*, in natural fillowite-type phosphates: Na-richest samples contain 3.3 Na and 1.0 Ca *pfu* (Na/Ca = 3.3), while Na-poorest samples, corresponding to johnsomervilleite from Loch Quoich, contain 2.1 Na and 1.6 Ca *pfu*
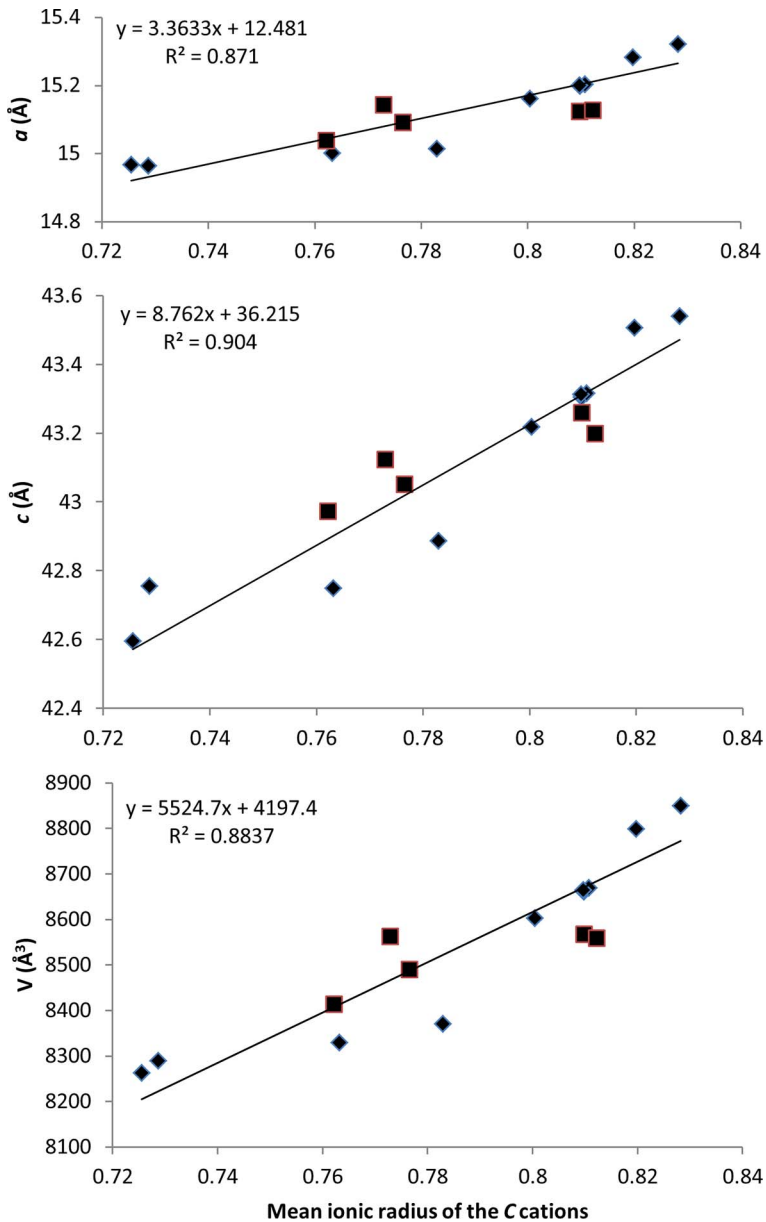
FIG. 6. Correlations between the unit-cell parameters of fillowite-type phosphates and the mean ionic radius of the C cations. The squares correspond to data from the present paper, while the diamonds correspond to literature data.

(Na/Ca = 1.31). As previously pointed out by Fransolet *et al.* (1998), the substitution mechanism, explaining the variations of the Na/Ca ratio of fillowite-type phosphates, is $Na^+ + Na^+ = Ca^{2+} + \square$. This mechanism is confirmed by the correlation of Figure 5A, with a slope of –1.83, fairly close to the theoretical value of –2.

Significant amounts of Fe^{3+} are frequently observed in fillowite-type phosphates, for example in the Sapucaia chladniite sample where Fe^{3+} attains 1.004 *apfu* (Table 1). As shown in Figure 5B, a correlation exists between the number of vacancies *pfu* and the Fe^{3+} content: Fe^{3+}-rich samples necessarily contain significant amounts of vacancies, while Fe^{3+}-poor

samples show variations of the vacancy content, certainly due to the $Na^+ + Na^+ = \square + Ca^{2+}$ substitution. The insertion of Fe^{3+} in the fillowite structure is consequently accompanied by the insertion of vacancies, in good agreement with the two possible substitution mechanisms $Na + M^{2+} = \square + Fe^{3+}$ (Fransolet *et al.* 1998) and $Mn^{2+} + 2\,Fe^{2+} = \square + 2\,Fe^{3+}$ (Hatert 2002).

Significant amounts of Al (max. 0.016 *apfu*) and Zn (max. 0.070 *apfu*) are also observed in the chemical analyses: Al substitutes for Fe^{3+} and Zn for the divalent cations Fe^{2+}, Mn, and Mg. Rare-earth elements occur at the $M(1)$ site of chladniite from Larsemann Hills, Antarctica [previously "stornesite-(Y)" samples], in amounts up to 0.170 Y and 0.005 Yb *pfu*. Potassium and Li substitute for Na and can attain 0.067 K *pfu* and 0.116 Li *pfu*. Water was observed by Fransolet *et al.* (1998) in natural samples and by Keller *et al.* (2006) in a synthetic compound in amounts reaching 0.25 H_2O *pfu*.

Variations of unit-cell parameters

Fransolet *et al.* (1998) observed a negative and strong correlation between the $(Fe + Mg)/(Fe + Mg + Mn)$ ratio of fillowite-type phosphates and their unit-cell parameters. This correlation, which has been extended to synthetic compounds by Hatert (2002) and Rondeux (2010), can be revised by considering the new data presented here. As shown in Figure 6, these correlations are fairly good, with correlation coefficients between 87 and 90%. The very large variations of the c unit-cell parameters, compared to those of the a unit-cell parameters, can be explained by the position of the cationic sites, forming chains parallel to **c**.

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