

Hydrothermal synthesis and crystal structure of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$, a new compound of fillowite structure type

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Abstract: The chemical compound $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$ was synthesized with a Tuttle pressure vessel at 800 °C and 1 kbar during experimental investigations on the conditions of fillowite formation. The crystal structure of a single-crystal, space group $R\bar{3}$ (No. 148), $a = 15.2741(9)$, $c = 43.334(3)$ Å, $Z = 6$, was determined from X-ray intensity data and refined up to $R_1 = 0.0728$ and $R_{1\{\text{FO} > 4\sigma(\text{FO})\}} = 0.0546$. The crystal structure of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$ is similar to the structure of fillowite, $\text{Na}_6\text{Ca}_3(\text{Mn},\text{Fe})_{21}(\text{PO}_4)_{18}$, but a significant difference between the synthetic H_2O containing compound and fillowite is the replacement of $(\text{Na}12)\text{O}_8^-$ by $\text{Mn}(\text{H}_2\text{O})_2\text{O}_5^-$ polyhedra, which form characteristic six-member rings. The coordination polyhedra around Na12 and Mn12 are so different that simple isomorphous substitution of Na12 by Mn12 is very unlikely, but whole six-member rings either of $(\text{Na}12)\text{O}_8^-$ or $(\text{Mn}12)(\text{H}_2\text{O})_2\text{O}_5^-$ polyhedra seem to be distributed statistically over the crystal structure. No indication for ordering, e.g. sheet by sheet, has been observed. $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$ is the first fillowite-like compound for which water is located in the structure from single-crystal study. This result is proved by infrared spectral data and indicates that water can play an essential role in the fillowite structure-type. Structural features of the synthetic compounds $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$, $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$ and fillowite are compared.

Key-words: $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$, crystal structure, fillowite, phosphate minerals, pegmatites.

Introduction

The name fillowite pertains to a phosphate mineral which has been described by Brush & Dana (1878) in the Branchville pegmatite, Connecticut, and which is well known to occur as an accessory phosphate in rare elements granitic pegmatites. The very complex and exciting crystal structure of this mineral has been determined by Araki & Moore (1981) and the general structural formula $\text{Na}_2\text{CaM}^{2+}_7(\text{PO}_4)_6$ ($M^{2+} = \text{Mn}, \text{Fe}$ or Mg), with $Z = 18$, was calculated from existing chemical analyses. Forty-five nonequivalent atoms in the asymmetric unit can be attributed to the very large unit cell of fillowite with $a = 15.282(2)$ and $c = 43.507(3)$ Å. Their atomic arrangement has been described by a hexagonal rod packing (Araki & Moore, 1981; Moore, 1981) and was also considered as an oxygen-stuffed derivate of $\alpha\text{-Fe}$ in $R\bar{3}c$ representation by Moore (1989), like glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$ (Moore, 1981, 1989).

Several new mineral species were also described in granitic pegmatites and in meteoritic rocks most likely having the fillowite structure type, thus extending the fillowite group. In pegmatites, the Mn-rich and the Fe^{2+} -rich end-members, with chemical compositions $\text{Na}_2\text{CaMn}_7(\text{PO}_4)_6$

and $\text{Na}_2\text{CaFe}_7(\text{PO}_4)_6$, are named fillowite and johnsomervilleite, respectively (Araki & Moore, 1981; Livingstone, 1980). In meteoritic rocks, chladniite, $\text{Na}_2\text{CaMg}_7(\text{PO}_4)_6$, is the Mg-rich equivalent of fillowite (McCoy *et al.*, 1994), whereas galileiite, $\text{NaFe}^{2+}_4(\text{PO}_4)_3$, corresponds to Ca-free johnsommervilleite (Olsen & Steele, 1997).

The complex chemistry of fillowite-type minerals was demonstrated by Fisher (1965), and the crystal chemistry of the fillowite-johnsommervilleite series was recently investigated in detail by Fransolet *et al.* (1998), starting from new chemical analyses performed on phosphates from Central Africa. These authors considered a crystallochemical formula $\text{Na}_5(\text{Ca}_2\text{Na})_{\Sigma=3}\text{M}_{22}(\text{PO}_4)_{18}$ for fillowite-type minerals, and emphasized the role of Ca, which can easily reach 1 among the 22 M cations in the formula. The occurrence of trivalent cations (Fe^{3+} , Al^{3+}) and of lattice vacancies are explained by the substitution mechanisms $\text{Na}^+ + M^{2+} \rightarrow \square + M^{3+}$, and $\text{Na}^+ + \text{Na}^+ \rightarrow \square + \text{Ca}^{2+}$. A correlation between the unit-cell parameters and the Mn content was also established (Fransolet *et al.*, 1998). The investigation of several fillowites and johnsommervilleites from Central Africa (Fransolet *et al.*, 1998) also demonstrated the petrogenetic significance of these phosphates. A paragenesis fil-

lowite + alluaudite, occurring as grains with a mosaic texture and without any reaction, indicates that these phosphates have crystallized together, and are probably of primary origin.

Experimental investigations were also performed on fillowite-type compounds. Domanskii *et al.* (1982) have synthesized the compound $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$ and published a structure determination with $R = 0.038$). Antenucci *et al.* (1996), have demonstrated the existence of a reversible alluaudite-fillowite polymorphism affecting $\text{NaCaCdMg}_2(\text{PO}_4)_3$. Recently, this experimental work was continued by Hatert (2002, 2004) and Hatert & Fransolet (2003), in order to better understand the crystal chemistry and the stability of fillowite-type compounds. Starting from the compositions $\text{NaMn}_3M^{2+}(\text{PO}_4)_3$ ($M^{2+} = \text{Mn, Ca, Mg, Fe}$), $\text{NaCaMnMg}_2(\text{PO}_4)_3$, and $\text{Na}_2\text{Cd}_2\text{Sc}(\text{PO}_4)_3$, these authors synthesized pure fillowite-type compounds by solid state reactions in air, and therefore demonstrated that Cd and Sc can easily be introduced in the fillowite structure. Hydrothermal experiments in the Na-Mn-Fe²⁺-Fe³⁺-P-O system (Hatert, 2002, 2004) enable the synthesis of fillowite-type compounds between 700 and 800 °C ($P = 1$ kbar), starting from the composition $\text{Na}_2\text{Mn}_2\text{Fe}^{3+}(\text{PO}_4)_3$, whereas the compound of nominal composition $\text{NaMn}_4(\text{PO}_4)_3$ was synthesized at 600 and 800 °C, $P = 3.5$ and 1 kbar, respectively. These preliminary results confirm the primary origin of fillowite, as already mentioned by Fransolet *et al.* (1998).

The aim of this paper is to describe the crystal structure of the synthetic fillowite-type compound $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$, obtained by Hatert (2002) at 800 °C and 1 kbar, starting from the composition $\text{NaMn}_4(\text{PO}_4)_3$. With its simple chemical starting composition, this phase corresponds to Ca- and Fe-free fillowite or to "Mn-galileiite" and turns out to be a very interesting compound for following systematic investigations on the structural chemistry of the fillowite-type minerals and compounds.

Experimental

Hydrothermal synthesis

The fillowite-type compound described in this study was synthesized under hydrothermal conditions, in the Laboratory of Mineralogy of the Ruhr-Universität Bochum, Germany. The starting material, of composition $\text{NaMn}_4(\text{PO}_4)_3$, was prepared by mixing $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Merck, Darmstadt, Germany, min. 99 %) and MnO (Alfa, Karlsruhe, Germany, 99.5 %) in the appropriate proportions. A solution of H_3PO_4 (ca. 80 %) was added in order to achieve stoichiometry and the mixture was homogenized in a mortar after evaporation. About 25 mg of the resulting residue was sealed into a gold tube with an outer diameter of 2 mm, and a length of 25 mm, containing 2 µl distilled water. The synthesis was carried out with a conventional hydrothermal apparatus with a horizontally oriented Tuttle-type pressure vessel (Tuttle, 1949), maintained at a temperature of 800 °C and a pressure of 1 kbar. After 14 days the sample was quenched to room temperature in a stream of cold air. The synthesized crystals were isometric and only of fillowite-type. Their diameter

was from 100 to 200 µm, and they showed a white to pinkish color.

The redox conditions encountered in the autoclave, which is made of hard steel, were very close to those controlled by the Ni-NiO oxygen fugacity buffer (O'Neill & Pownceby, 1993). Such reducing conditions strongly favor the occurrence of Mn²⁺ instead of Mn³⁺.

Electron-microprobe analyses

The electron-microprobe analyses were performed at the Louvain-la-Neuve University, Belgium, with a CAMECA SX50 (Analyst J. Wautier). The accelerating voltage was 15 kV and the probe current was 20 nA. The standards used were the Kabira graffonite (Fransolet, 1975) (Mn, P) and oligoclase (Na). The average of 8 point analyses gave: Na₂O: 6.22(6), MnO: 53.74(51), P₂O₅: 40.43(33), total: 100.39 wt. %. The chemical formula, calculated from the microprobe analyses on the basis of 18 P atoms per formula unit, is $\text{Na}_{6.35}\text{Mn}_{23.94}(\text{PO}_4)_{18}$.

Infrared spectroscopy

The infrared spectrum of the title compound (Fig. 1) was recorded with a Nicolet NEXUS spectrometer, from 32 scans with a 1 cm⁻¹ resolution, between 400 and 4000 cm⁻¹. The sample was prepared by thoroughly mixing 2 mg of sample with KBr in order to obtain a 150 mg homogeneous pellet which was subsequently dried for several hours at 120 °C. To prevent water contamination, the measurement was performed under a dry air purge.

Structure determination

A tiny crystal was measured on a Nonius-κ-CCD diffractometer equipment with monochromatized Mo-Kα radiation. The absorption was corrected using the HABITUS program (Herrendorf & Bärnighausen, 1997) for 621 equivalents and 99 unique reflections. All essential measuring parameters are given in Table 1.

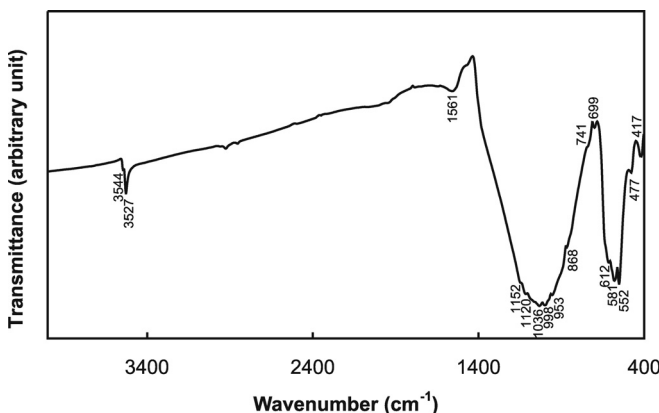


Fig. 1. Infrared spectrum of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$.

Table 1. Experimental details and crystallographic data for the synthetic fillowite-type compound, $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$.

Crystal data			
Space Group	$R\bar{3}$ (No. 148)	Z	6
a [Å]	15.2741(9)	$D_{\text{calc.}}$ [g/cm ³]	3.61
c [Å]	43.3345(31)	μ [mm ⁻¹]	6.65
V [Å ³]	87554(1)	Size of crystal [mm]	0.3, 0.2, 0.2
Intensity measurements			
Diffractometer	Nonius K-CCD	Observed reflections	42889
Monochromator	graphite	Unique reflections	7302
Radiation	Mo-K α	R_{int}	0.0697
$2\Theta_{\text{max}}$ [°]	65.96	R_{σ}	0.0470
$h_{\text{min.}}, h_{\text{max.}}$	-23, 23	Temperature [°C]	25
$k_{\text{min.}}, k_{\text{max.}}$	-23, 23	F(000)	9082
$l_{\text{min.}}, l_{\text{max.}}$	-66, 66		
Structure determination and refinement			
Reflections used	7300	$wR_2(\text{all})$	0.1504
Reflections with $F_0 > 4\sigma(F_0)$	5165	Weighting parameters	0.1063
Parameters refined	380	GooF	0.946
Extinction	0.00052	$(\Delta\rho)_{\text{max}}$ [e/Å ³]	2.15
R_1 (7302 reflections after merging)	0.0728	$(\Delta\rho)_{\text{min}}$ [e/Å ³]	-1.37
$R_1(F)$ ($F_0 > 4\sigma(F_0)$)	0.0546	R_{ms} [e/Å ³]	0.30
$R_1(\text{all})$	0.0754		

Systematic absences and reflection statistics indicate the space group $R\bar{3}$ (No. 148) without any systematic absence violations. The structure was solved by direct methods with the program package SHELXTL (Sheldrick, 1996) yielding the position of all non-H atoms. Subsequent structure refinements of the positional and anisotropic displacement parameters on F^2 with the SHELXL97 program (Sheldrick, 1997) converged for 7302 unique reflections after merging to $R1 = 8.08\%$. The result confirms, as expected, close similarities to the fillowite structure (Keller *et al.*, 2001). A first remarkable exception, however, is the oxygen position $O25$ in excess.

The R-values could be further improved up to $R1 = 7.46\%$ by refinement of the site occupancy factors for Na12, Na13 and Na31. All other cation sites are occupied by one atom only, either Mn or Na, virtually without any isomorphous substitution. The structure refinement was completed with $R1 = 7.28$ for 7300 unique reflections after merging by use of the least-squares constraints EADP and EXYZ for the pairs of atoms Na12/Mn12, Na13/Mn13 and Na31/Mn31. The substitution of Na12 by Mn12 on site $M12$ and its individual coordination sphere could be further improved with the PART option of SHELXL97.

According to the site occupancy factors, the structural formula of the title compound is $\text{Na}(\text{Na}_{5.38}\text{Mn}_{1.62})_{\Sigma 7.00}\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.48\text{H}_2\text{O}$, considering the additional $O25$ as H_2O (see below). If all manganese is divalent, this formula is not charge-balanced, and shows a deficit of 0.38 positive charges. This negligible deficit could be explained by the presence of small amounts of Mn^{3+} , which can not be confirmed without a detailed spectroscopic investigation. The formula calculated from the electron-microprobe analyses, $\text{Na}(\text{Na}_{5.35}\text{Mn}_{1.65})_{\Sigma 7.00}\text{Mn}_{22.29}(\text{PO}_4)_{18}$, is in agreement with the calculated structural formula.

Further details of the structure determination and refinement are summarized in Table 1. The final atomic coordinates and equivalent displacement parameters are given in Tables 2 and 3, respectively. Selected bond lengths and angles are given in Table 4 and 5, respectively.

Results and discussions

Description and discussion of the crystal structure

The crystal structure of synthetic $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$ is, as expected, quite similar to the structure of fillowite, $\text{Na}_6\text{Ca}_3(\text{Mn},\text{Fe})_{21}(\text{PO}_4)_{18}$, of Araki & Moore (1981). Interesting new structural features can be attributed to the different chemistry of the synthetic compound. For easy comparison, the indications of atom sites used in this paper are as far as possible, identical with those given by Araki & Moore (1981), and furthermore, the crystal structure of the synthetic compound will be described and discussed closely related and referred to that of fillowite by Araki & Moore (1981). It turns out to be especially convenient to adopt the scheme of hexagonal rod-packing, which was created by Moore (1981), to describe and discuss the extraordinary complex topology (general structural architectures) of fillowite.

The hexagonal rod-packing of Moore (1981) consists of three rods parallel to the c -axis. The rods are composed of sequences of linked coordination polyhedra, which can be interrupted by empty spaces. Some of them are called "ordered vacancies" by Moore (1981) and characterized with \square in formula and figures. With respect to the enlarged structural flexibility discussed in this paper, however, it seems to be convenient to use the term "ordered vacancy" and the sign \square for any empty space into a rod (The term "ordered

Table 2. Positional and isotropic thermal parameters (\AA^2) for the synthetic fillowite-type compound, $\text{Na}(\text{Na},\text{Mn})_7\text{-Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$.

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mn1	0	0	0	0.0256(3)
Mn2	0	0	1/2	0.0162(3)
Mn3	0	0	0.10018(3)	0.0179(2)
Mn4	0	0	0.32434(3)	0.0158(2)
Mn5	0	0	0.39899(3)	0.0172(2)
Mn6	0.42812(5)	0.24537(5)	0.05085(2)	0.0210(1)
Mn7	0.11219(5)	0.57486(5)	0.03720(2)	0.0206(1)
Mn8	0.00445(5)	0.32554(5)	0.08186(1)	0.0177(1)
Mn9	0.26385(5)	0.32804(5)	0.08524(2)	0.0195(1)
Mn10	0.57335(6)	0.08199(5)	0.12377(2)	0.0238(2)
Mn11	0.22349(5)	0.10704(5)	0.13345(2)	0.0209(1)
Na12*	0.2758(8)	0.3010(8)	0.0003(2)	0.0307(9)
Mn12*	0.2502(4)	0.2738(4)	0.00287(9)	0.0307(9)
Na13*	0	0	0.17489(6)	0.0210(5)
Mn13*	0	0	0.17489(6)	0.0210(5)
Na21	0	0	0.24893(8)	0.0313(8)
Na31*	0.0829(2)	0.4296(2)	0.16468(4)	0.0361(9)
Mn31*	0.0829(2)	0.4296(2)	0.16468(4)	0.0361(9)
P1	0.19002(8)	0.43219(8)	0.02818(2)	0.0171(2)
P2	0.53382(8)	0.11384(8)	0.03978(2)	0.0176(2)
P3	0.54159(8)	0.09200(8)	0.19919(3)	0.0171(2)
P4	0.21748(8)	0.12237(8)	0.20971(3)	0.0173(2)
P5	0.22252(8)	0.46132(8)	0.22164(2)	0.0153(2)
P6	0.46731(8)	0.22037(8)	0.27971(3)	0.0189(2)
O1	0.1537(4)	0.3801(3)	-0.00295(9)	0.0371(9)
O2	0.2607(3)	0.5484(3)	0.02560(8)	0.0288(7)
O3	0.2516(3)	0.3903(4)	0.0438(1)	0.0358(9)
O4	0.0988(3)	0.4179(3)	0.04655(8)	0.0249(6)
O5	0.4609(2)	0.1271(2)	0.06093(8)	0.0219(6)
O6	0.5562(3)	0.0330(2)	0.05233(8)	0.0236(6)
O7	0.6371(3)	0.2142(2)	0.03960(8)	0.0242(6)
O8	0.4887(3)	0.0896(3)	0.00756(8)	0.0315(8)
O9	0.5391(3)	0.0315(3)	0.17090(8)	0.0272(7)
O10	0.6265(2)	0.2038(2)	0.19680(8)	0.0206(6)
O11	0.4395(2)	0.0897(2)	0.20210(8)	0.0223(6)
O12	0.5519(3)	0.0422(2)	0.22887(8)	0.0219(6)
O13	0.2346(3)	0.0796(3)	0.18002(9)	0.0309(8)
O14	0.1233(2)	0.1334(3)	0.20714(9)	0.0260(7)
O15	0.8902(2)	0.2427(2)	0.11622(8)	0.0221(6)
O16	0.1996(3)	0.0430(3)	0.23475(8)	0.0254(7)
O17	0.2673(3)	0.5280(3)	0.19369(8)	0.0272(7)
O18	0.1045(2)	0.3993(2)	0.21904(7)	0.0205(6)
O19	0.2542(3)	0.3795(2)	0.22192(8)	0.0212(6)
O20	0.2486(3)	0.5209(2)	0.25210(8)	0.0229(6)
O21	0.5212(3)	0.2538(3)	0.2486(1)	0.0331(8)
O22	0.3833(3)	0.1071(3)	0.27509(8)	0.0243(6)
O23	0.4132(3)	0.2799(3)	0.2869(1)	0.0325(8)
O24	0.5330(4)	0.2237(4)	0.3061(1)	0.047(1)
O25*	0.585(1)	0.129(1)	0.3140(4)	0.017(5)

* Occupancy factors: Na(12)/Mn(12) = 0.58(2)/0.42(2); Na(13)/Mn(13) = 0.28(1)/0.05(1); Na(31)/Mn(31) = 0.93(2)/0.07(2); O(25) = 0.16(2).

Table 3. Anisotropic thermal parameters (\AA^2) for the synthetic fillowite-type compound, $\text{Na}(\text{Na},\text{Mn})_7\text{-Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$.

Sites	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Mn1	0.0282(5)	0.0282(5)	0.0202(8)	0	0	0.0141(3)
Mn2	0.0167(4)	0.0167(4)	0.0153(6)	0	0	0.0083(2)
Mn3	0.0177(3)	0.0177(3)	0.0182(5)	0	0	0.0088(1)
Mn4	0.0166(3)	0.0166(3)	0.0142(5)	0	0	0.0083(1)
Mn5	0.0172(3)	0.0172(3)	0.0174(5)	0	0	0.0086(1)
Mn6	0.0192(3)	0.0275(3)	0.0179(3)	-0.0007(2)	-0.0002(2)	0.0129(3)
Mn7	0.0196(3)	0.0241(3)	0.0183(3)	0.0008(2)	-0.0008(2)	0.0109(2)
Mn8	0.0169(3)	0.0189(3)	0.0172(3)	0.0018(2)	0.0014(2)	0.0090(2)
Mn9	0.0213(3)	0.0196(3)	0.0173(3)	-0.0003(2)	-0.0006(2)	0.0099(2)
Mn10	0.0251(3)	0.0163(3)	0.0288(4)	0.0032(2)	0.0087(3)	0.0094(2)
Mn11	0.0192(3)	0.0194(3)	0.0245(3)	0.0033(2)	0.0045(2)	0.0098(2)
Na12	0.033(2)	0.039(2)	0.025(1)	-0.006(1)	-0.002(1)	0.022(2)
Mn12	0.033(2)	0.039(2)	0.025(1)	-0.006(1)	-0.002(1)	0.022(2)
Na13	0.0226(7)	0.0226(7)	0.018(1)	0	0	0.0113(3)
Mn13	0.0226(7)	0.0226(7)	0.018(1)	0	0	0.0113(3)
Na21	0.037(1)	0.037(1)	0.020(2)	0	0	0.0186(6)
Na31	0.058(2)	0.052(1)	0.021(1)	0.0050(8)	0.0022(8)	0.044(1)
Mn31	0.058(2)	0.052(1)	0.021(1)	0.0050(8)	0.0022(8)	0.044(1)
P1	0.0193(4)	0.0181(4)	0.0144(4)	0.0010(3)	0.0007(3)	0.0097(4)
P2	0.0214(5)	0.0169(4)	0.0154(5)	0.0017(3)	0.0022(4)	0.0103(4)
P3	0.0177(4)	0.0159(4)	0.0170(5)	-0.0007(3)	0.0003(3)	0.0078(4)
P4	0.0171(4)	0.0164(4)	0.0181(5)	-0.0017(3)	-0.0026(4)	0.0083(4)
P5	0.0170(4)	0.0147(4)	0.0141(4)	0.0005(3)	-0.0001(3)	0.0078(3)
P6	0.0166(4)	0.0207(5)	0.0203(5)	-0.0011(4)	-0.0003(4)	0.0101(4)
O1	0.059(3)	0.025(2)	0.019(2)	-0.003(1)	-0.004(2)	0.015(2)
O2	0.034(2)	0.024(2)	0.018(2)	0.000(1)	0.001(1)	0.007(1)
O3	0.035(2)	0.050(2)	0.034(2)	0.015(2)	0.008(2)	0.030(2)
O4	0.021(1)	0.026(2)	0.028(2)	0.002(1)	0.002(1)	0.012(1)
O5	0.021(1)	0.021(1)	0.023(1)	0.001(1)	0.006(1)	0.010(1)
O6	0.024(1)	0.019(1)	0.028(2)	0.001(1)	-0.004(1)	0.011(1)
O7	0.023(1)	0.020(1)	0.029(2)	0.005(1)	0.006(1)	0.011(1)
O8	0.049(2)	0.032(2)	0.018(2)	-0.002(1)	-0.003(1)	0.024(2)
O9	0.034(2)	0.023(1)	0.021(2)	-0.003(1)	0.005(1)	0.012(1)
O10	0.020(1)	0.017(1)	0.022(1)	0.000(1)	0.003(1)	0.007(1)
O11	0.018(1)	0.021(1)	0.028(2)	0.003(1)	-0.001(1)	0.009(1)
O12	0.023(1)	0.021(1)	0.023(1)	0.002(1)	-0.002(1)	0.011(1)
O13	0.042(2)	0.033(2)	0.022(2)	-0.009(1)	-0.005(1)	0.022(2)
O14	0.018(1)	0.025(1)	0.036(2)	-0.002(1)	-0.006(1)	0.011(1)
O15	0.022(1)	0.023(1)	0.024(2)	0.004(1)	0.004(1)	0.013(1)
O16	0.034(2)	0.022(1)	0.021(2)	0.001(1)	-0.005(1)	0.014(1)
O17	0.035(2)	0.021(1)	0.022(2)	0.004(1)	0.004(1)	0.011(1)
O18	0.019(1)	0.022(1)	0.020(1)	-0.002(1)	0.000(1)	0.009(1)
O19	0.025(1)	0.021(1)	0.020(1)	-0.001(1)	-0.001(1)	0.013(1)
O20	0.030(2)	0.017(1)	0.020(1)	-0.003(1)	-0.003(1)	0.011(1)
O21	0.024(2)	0.035(2)	0.034(2)	0.004(2)	0.009(1)	0.010(1)
O22	0.022(1)	0.021(1)	0.027(2)	-0.001(1)	0.004(1)	0.009(1)
O23	0.034(2)	0.032(2)	0.041(2)	0.007(2)	0.006(2)	0.023(2)
O24	0.051(3)	0.066(3)	0.043(2)	-0.027(2)	-0.028(2)	0.045(2)
O25	0.03(1)	0.03(1)	0.010(8)	0.006(6)	0.001(6)	0.021(8)

The anisotropic displacement factor exponent is defined as: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

Table 4. Interatomic distances (Å) for the synthetic fillowite-type compound, Na(Na,Mn)₇Mn₂₂(PO₄)₁₈·0.5H₂O.

Mn1-O24* × 6	2.224(4)	Mn2-O17* × 6	2.177(3)	Mn3-O10* × 3	2.359(3)	Mn4-O2* × 3	2.177(4)
Mean	2.224	Mean	2.177	Mn3-O21* × 3	2.039(4)	Mn4-O7* × 3	2.110(3)
				Mean	2.199	Mean	2.144
Mn5-O2* × 3	2.345(4)	Mn6-O1	2.172(4)	Mn7-O2	2.545(4)	Mn8-O4	2.091(4)
Mn5-O20* × 3	2.051(3)	Mn6-O5	2.147(3)	Mn7-O2'	2.648(4)	Mn8-O5	2.265(3)
Mean	2.198	Mn6-O6	2.736(3)	Mn7-O3	2.489(5)	Mn8-O12	2.228(3)
		Mn6-O7	2.134(4)	Mn7-O4	2.338(4)	Mn8-O15	2.158(3)
		Mn6-O16	2.167(4)	Mn7-O6	2.055(3)	Mn8-O19	2.209(3)
		Mn6-O22	2.106(3)	Mn7-O8	2.044(4)	Mn8-O23	2.262(4)
		Mean	2.244	Mn7-O20	2.156(4)	Mean	2.202
				Mean	2.325		
Mn9-O3	2.083(4)	Mn10-O9	2.154(4)	Mn11-O10	2.160(3)	Mn12-O1	2.433(7)
Mn9-O11	2.286(3)	Mn10-O13	2.625(4)	Mn11-O11	2.062(3)	Mn12-O3	2.507(7)
Mn9-O12	2.217(3)	Mn10-O14	2.071(4)	Mn11-O13	2.086(4)	Mn12-O22	2.621(6)
Mn9-O18	2.086(3)	Mn10-O16	2.146(4)	Mn11-O15	2.087(3)	Mn12-O23	2.241(7)
Mn9-O22	2.082(3)	Mn10-O18	2.217(3)	Mn11-O21	2.355(4)	Mn12-O24	2.453(7)
Mean	2.151	Mn10-O19	2.312(3)	Mean	2.150	Mn12-O25	2.26(2)
		Mean	2.254			Mn12-O25'	2.33(2)
						Mean	2.406
Na12-O1	2.38(1)	Na13-O10* × 3	2.417(4)	Na21-O7* × 3	2.542(4)	Na31-O9	2.369(4)
Na12-O1'	2.68(1)	Na13-O14* × 3	2.411(4)	Na21-O14* × 3	2.673(4)	Na31-O9'	2.574(4)
Na12-O3	2.47(1)	Mean	2.414	Na21-O16* × 3	2.847(4)	Na31-O11	2.802(4)
Na12-O4	2.90(1)			Mean	2.687	Na31-O17	2.473(4)
Na12-O8	2.587(9)					Na31-O17'	2.746(5)
Na12-O22	2.77(1)					Na31-O18	2.455(4)
Na12-O23	2.25(1)					Na31-O19	2.468(4)
Na12-O24	2.835(9)					Mean	2.555
Mean	2.609						
P1-O1	1.523(4)	P2-O5	1.532(3)	P3-O9	1.524(4)	P4-O13	1.525(4)
P1-O2	1.554(4)	P2-O6	1.535(3)	P3-O10	1.546(3)	P4-O14	1.534(3)
P1-O3	1.534(4)	P2-O7	1.556(4)	P3-O11	1.547(3)	P4-O15	1.546(3)
P1-O4	1.524(4)	P2-O8	1.519(4)	P3-O12	1.542(3)	P4-O16	1.546(4)
Mean	1.534	Mean	1.536	Mean	1.540	Mean	1.538
P5-O17	1.508(4)	P6-O21	1.530(4)				
P5-O18	1.566(3)	P6-O22	1.568(4)				
P5-O19	1.551(3)	P6-O23	1.536(4)				
P5-O20	1.538(3)	P6-O24	1.506(4)				
Mean	1.541	Mean	1.535				

* For the sake of simplicity, symmetrically equivalent atoms are considered under the same label.

Table 5. Bond valence calculations for $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$ according to the equation $s = \exp[(R_0 - R_M)/0.37]$ and the empirical values of Brown & Altermatt (1985).

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	O14	O15	O16	O17	O18	O19	O20	O21	O22	O23	O24	O25	Sum	
Mn1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	1.86
Mn2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.35	-	-	-	-	-	-	-	-	-	2.10
Mn3	-	-	-	-	-	-	-	-	-	0.21	-	-	-	-	-	-	-	-	-	-	0.51	-	-	-	-	-	2.16
Mn4	-	0.35	-	-	-	-	0.42	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.31
Mn5	-	0.22	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.49	-	-	-	-	-	2.13
Mn6	0.36	-	-	-	0.38	0.08	0.39	-	-	-	-	-	-	-	-	0.36	-	-	-	-	-	-	0.43	-	-	-	2.00
Mn7	-	0.13	0.15	0.23	-	0.49	-	0.50	-	-	-	-	-	-	-	-	-	-	-	-	0.37	-	-	-	-	-	1.97
Mn8	-	-	-	0.44	0.28	-	-	-	-	-	-	0.31	-	-	0.37	-	-	-	0.32	-	-	-	0.28	-	-	-	2.00
Mn9	-	-	0.45	-	-	-	-	-	-	-	0.26	0.32	-	-	-	-	-	0.45	-	-	-	0.45	-	-	-	-	1.93
Mn10	-	-	-	-	-	-	-	-	0.37	-	-	-	0.11	0.47	-	0.38	-	0.32	0.24	-	-	-	-	-	-	-	1.89
Mn11	-	-	-	-	-	-	-	-	-	0.37	0.48	-	0.45	-	0.45	-	-	-	-	-	-	0.22	-	-	-	-	1.97
M12*	0.20*	-	0.16*	0.05* ¹	-	-	-	0.12* ¹	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.09*	0.30*	0.11*	0.28* ²	1.07 ¹⁾
	0.09* ¹																									0.23* ²	1.42 ²⁾
Na13	-	-	-	-	-	-	-	-	-	0.19	-	-	-	0.19	-	-	-	-	-	-	-	-	-	-	-	-	1.14
Na21	-	-	-	-	-	-	0.14	-	-	-	-	-	-	0.10	-	0.06	-	-	-	-	-	-	-	-	-	-	0.90
Na31	-	-	-	-	-	-	-	-	0.22	-	0.07	-	-	-	-	-	0.16	0.17	0.17	-	-	-	-	-	-	-	0.99
									0.12								0.08										
P1	1.30	1.20	1.23	1.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.99
P2	-	-	-	-	1.27	1.26	1.19	1.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.03
P3	-	-	-	-	-	-	-	-	1.30	1.22	1.21	1.24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.97
P4	-	-	-	-	-	-	-	-	-	-	-	-	1.30	1.26	1.22	1.22	-	-	-	-	-	-	-	-	-	-	5.00
P5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.35	1.16	1.21	1.24	-	-	-	-	-	-	4.96
P6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.28	1.15	1.25	1.36	-	5.04
Sum	1.95	2.00	1.99	1.98	1.93	1.83	2.14	1.93	2.01	1.99	2.02	1.87	1.86	2.02	2.04	2.02	1.94	2.10	1.94	2.10	2.01	2.12	1.83	1.78	0.51		

*: M12 = 0.58 Na + 0.42 Mn; *¹: belongs only to Na12; *²: belongs only to Mn12; ¹⁾: sum calculated only for Na12; ²⁾: sum calculated only for Mn12

vacancy” is restricted to a distinct rod and should not be used for any other empty crystallographic site.) In the following, the terms rod I, rod II and rod III are defined as initially given by Araki & Moore (1981), but attention must be taken about the renaming of rods by Moore (1989). The rod coordinates in the x-y plane and in the asymmetric unit are: Rod I = (0, 0), parallel to the threefold axis; rod II = (1/3, 1/3), parallel to the 3_1 axis; rod III = (2/9, 1/9), at the nodes of fairly regular 6_3 nets (Moore, 1981, Fig. 5a).

The three rods of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$ are composed as described below. Different site occupation compared with fillowite (Araki & Moore, 1981) or with $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$ (Domanskii *et al.*, 1982) are marked by bold prints.

Rod I consists of a sequence of face-sharing coordination polyhedra of Mn and Na. They are interrupted by “ordered vacancies” □, which have not been considered by Araki & Moore (1981) and Moore (1981, 1989):

^{VI}Mn1-□-^{VI}Mn3-^{VI}Na13-^{IX}Na21-^{VI}Mn4-^{VI}Mn5-□-^{VI}Mn2-□-^{VI}Mn5-^{VI}Mn4-^{IX}Na21-^{VI}Na13-^{VI}Mn3-□- (Fig. 2). Whereas this sequence differs mainly due to the replacement of Fe^{2+} by Mn^{2+} from fillowite, a remarkable feature of $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$ (Domanskii *et al.*, 1982) is an “ordered vacancy” □ instead of Na13 (\equiv Na1): ^{VI}Ca2-□-^{VI}Mg1-□-^{IX}Na2-^{VI}Mn2-^{VI}Mg3-□-^{VI}Ca3-□-^{VI}Mg3-^{VI}Mn2-^{IX}Na2-□-^{VI}Mg1-□-.

Rod II of the title compound consists of a sequence of corner- and edge-sharing polyhedra:

[^{VIII}Na12 or ^{VIII}Mn12]-^VMn9-^{VII}Na31-^{VI}Mn8-[^{VIII}Na12 or ^{VII}Mn12]-^VMn9-^{VII}Na31-^{VI}Mn8-[^{VIII}Na12 or ^{VIII}Mn12]-

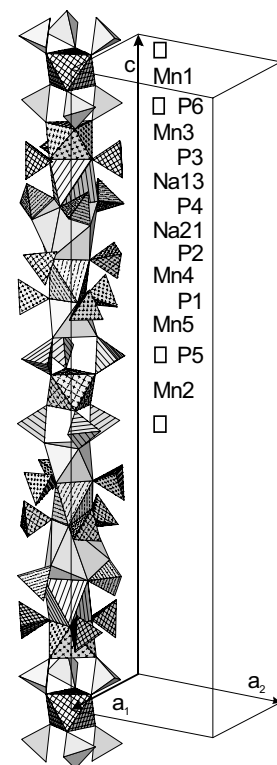


Fig. 2. Rod I of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$ is developed along the three-fold axis. Rod I consists of a sequence of face-sharing coordination polyhedra of cations, either Mn or Na, interrupted empty positions. The $[\text{PO}_4]$ -tetrahedra belong to different rods III.

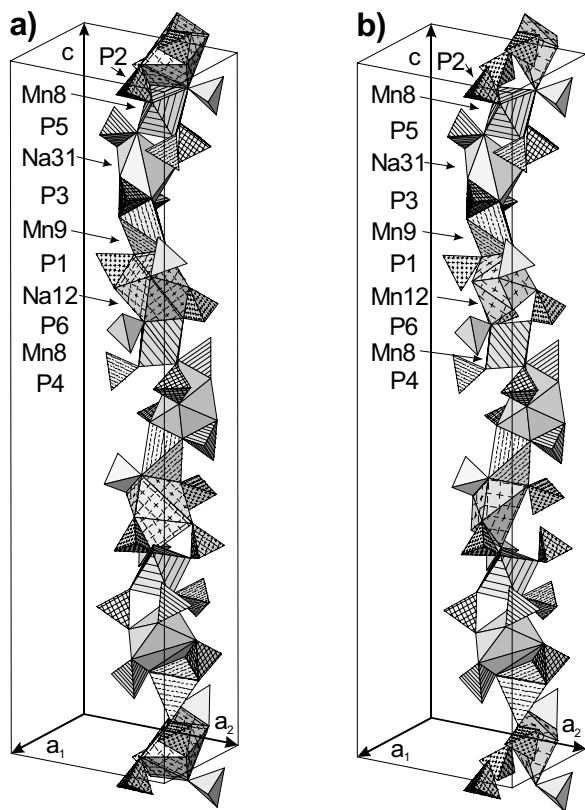


Fig. 3. Clinographic view of rod II developed along the three-fold screw axes. The coordination polyhedra of Mn and Na share common edges and vertices. The $[\text{PO}_4]$ tetrahedra belong again to rods III. Attention should be given to the structural differences caused by Na12 and Mn12 in Fig. 3a and Fig. 3b, respectively.

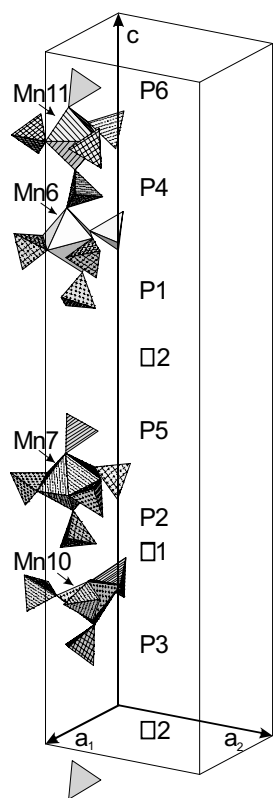


Fig. 4. Rod III consists of $[\text{PO}_4]$ tetrahedra and coordination polyhedra of Mn as well. Three different clusters of polyhedra, separated by quite large distances, form a chain parallel to the c -axis. The $[\text{PO}_4]$ tetrahedra surrounding the cations Mn belong to different other rods III.

$^{\text{V}}\text{Mn}9\text{--}^{\text{VII}}\text{Na}31\text{--}^{\text{VI}}\text{Mn}8\text{--}$ (Fig. 3). The occurrence of either $\text{Na}12\text{O}_8\text{--}$ or $\text{Mn}12(\text{H}_2\text{O})_2\text{O}_5\text{--}$ polyhedra is a most remarkable difference between $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$ (synthetic chladniite), and several unpublished Ca- and Fe-free synthetic compounds. This feature is extensively described and discussed below!

Rod III is rather similar for the synthetic compounds under discussion. The sequence includes all PO_4 tetrahedra, some coordination polyhedra of Mn (title compound) or Mg ($\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$) and ordered vacancies of small (\square_1) and large (\square_2) size: $\text{P}6\text{--}\square_2\text{--P}3\text{--}^{\text{VI}}\text{Mn}10\text{--}\square_1\text{--P}2\text{--}^{\text{VII}}\text{Mn}7\text{--P}5\text{--}\square_2\text{--P}1\text{--}^{\text{VII}}\text{Mn}6\text{--P}4\text{--}^{\text{V}}\text{Mn}11\text{--}$ (Fig. 4).

The structural characteristic of the title compound, compared with fillowite, is mainly a few higher coordination numbers and the additional ordered vacancy \square_1 .

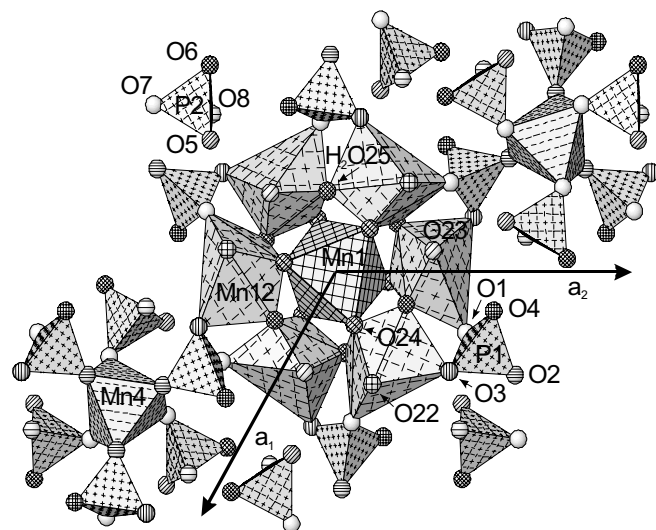
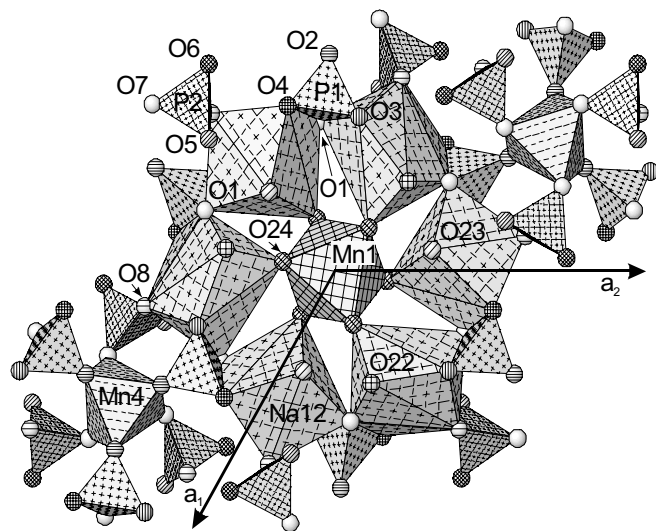


Fig. 5. Sheet I of $\text{Na}(\text{Na},\text{Mn})_7\text{--Mn}_{22}(\text{PO}_4)_{18}\cdot 0.5\text{H}_2\text{O}$ at $c \sim 0$ projected down the c -axis. Attention should be given to the rather different six-member rings of either Na12 (a) or Mn12 (b). Whereas the $(\text{Na}12)\text{O}_8$ polyhedra are linked to each other by two O1, those of $(\text{Mn}12)(\text{H}_2\text{O})_2\text{O}_5$ by $\text{H}_2\text{O}25$, only. The $(\text{Na}12)\text{O}_8$ polyhedra are additionally with the $(\text{P}1)\text{O}_4$ tetrahedra by O1-O3- and O1-O4-edges. The $(\text{Mn}12)(\text{H}_2\text{O})_2\text{O}_5$ polyhedra, however, only by O1 and O3 vertices.

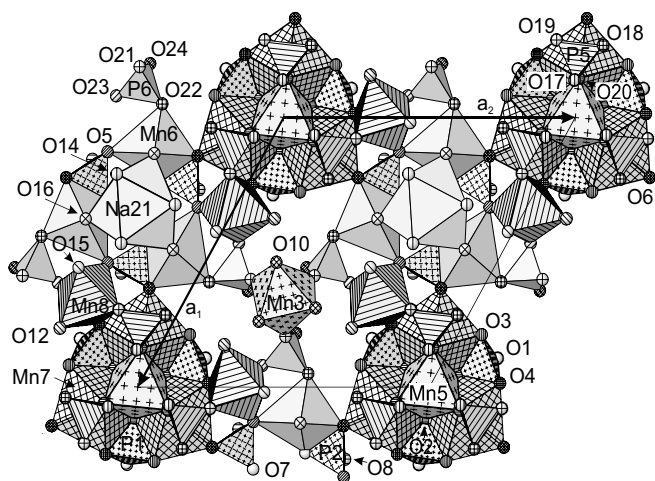


Fig. 6. Sheet 2 of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$ at about $0 \leq c < 1/12$, projected down the c -axis. Densely packed clusters consisting of $(\text{Mn}5)\text{O}_6$ octahedron, three pentagonal bi-pyramids of $(\text{Mn}7)\text{O}_7$ as well as $(\text{P}1)\text{O}_4$ and $(\text{P}5)\text{O}_4$ tetrahedra are developed at the edges of the unit cell.

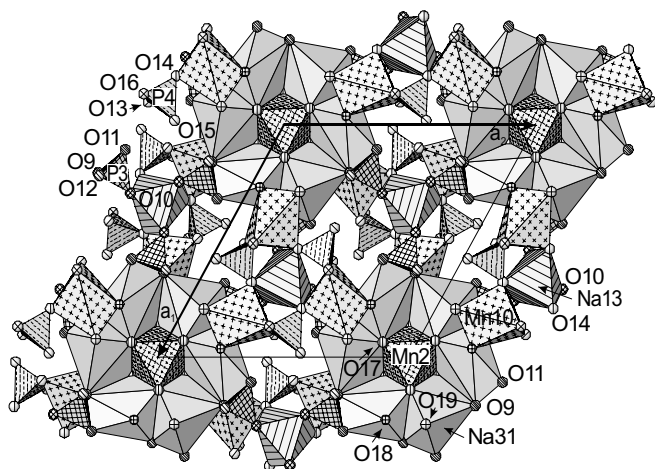


Fig. 7. Sheet 3 of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$ is a partial section at about $1/12 \leq c \leq 2/12$, projected down the c -axis.

The cation positions $M1$ to $M11$ of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$ are exclusively occupied by Mn^{2+} ions (Fig. 5–7). There is no substitution, neither by Na nor by Fe or Ca as for fillowite. $\text{Mn}1$ to $\text{Mn}5$ and $\text{Mn}8$ are clearly six-coordinated, forming either regular octahedra (trigonal antiprism) or more or less strongly distorted polyhedra in its appearance between an octahedron ($\text{Mn}8$) and a trigonal prism ($\text{Mn}4$) with Mn–O distances less than 2.36 Å (Table 4).

Whereas $\text{Mn}9$ and $\text{Mn}11$ are obviously five-coordinated with Mn–O bonds up to 2.355 Å, the coordination spheres of $\text{Mn}6$ and $\text{Mn}10$ are characterized by one much longer Mn–O bond of 2.736 and 2.625 Å, respectively. Although such long distances seem to be doubtful, the result of bond valence calculations (Table 5) gave positive arguments for six-coordination of both $\text{Mn}6$ and $\text{Mn}10$. A continuous sequence of bond-distances from 2.044 to 2.648 are, additional to bond valence calculations, clear evidence for CN = 7 of $\text{Mn}7$ and $\text{Mn}12$ (Table 2 and 5). It should be noted that the mean Mn–O distances as well as the Na–O distances of Table 4 differ very

little from those given by Araki & Moore (1981) and even the full substitution of Mn by Fe causes only small differences of about 0.011 and 0.024 Å. Compared with $\text{Mg}(\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18})$, the differences caused by the substitution of Mn by either Mg or Ca are certainly larger (either about -0.1 or $+0.1$ Å), but the coordination numbers are, with one exception (${}^{\text{VII}}\text{Mn}7$ vs. ${}^{\text{VI}}\text{Mg}4$), identical and even the coordination polyhedra display great similarity, e.g. three short and three long distances ($\text{Mn}3$, $\text{Mn}5$, $\text{Mn}7$ vs. $\text{Mg}1$, $\text{Mg}3$, $\text{Mg}4$) or a rather long bond distance ($\text{Mn}6$ vs. $\text{Mg}7$).

The coordination numbers of ${}^{\text{VI}}\text{Na}13$ (trigonal antiprism) and ${}^{\text{VII}}\text{Na}31$ (pentagonal bipyramid) are the same in the structures of fillowite and $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$, only the coordination sphere of $\text{Na}21$ is enlarged by a long Na–O bond of 2.847 Å to CN = 9 for the synthetic compound, as proved by the result of bond valence calculations (Table 5). An “ordered vacancy” instead of $\text{Na}13$ is a significant feature of $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$! For this and other reasons, we add further “ordered vacancies” to Rod I and III, although they may have unusual coordination spheres, but they are not excluded as possible cation positions according our experiences, for instance with minerals and compounds of the alluaudite structure-type (Keller *et al.*, 1981, Keller & Hess 1988; Riffel *et al.*, 1985; Antenucci *et al.*, 1996; Hatert, 2004). The “ordered vacancies” of Rod I (Fig. 2), for example, provide a triple-capped trigonal prism that may be suitable for a mono-valent cation coordinated by 6O of the surrounding PO_4 tetrahedra and additional $3\text{H}_2\text{O}$ (e.g. located above and below $\text{Mn}1$ and $\text{Mn}2$ in Fig. 5 and 7, respectively).

Remarkable consequences result from the substitution of Ca^{2+} (+ Na^+) by Mn^{2+} (+ Na^+) on the position Ca of Araki & Moore (1981) ($\equiv \text{Ca}1$ of Domanskii *et al.* 1982) and $M12$ (this paper), respectively. Whereas the coordination spheres of Na^+ and Ca^{2+} seem to be compatible in fillowite, Na^+ and Mn^{2+} on the same position of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$ causes serious structural deviations and the appearance of an additional oxygen ($\text{O}25 \equiv \text{H}_2\text{O}$), as discussed below. While the eight-coordinated $\text{Na}12$ is bonded to the same O^{2-} in both other structures with virtually identical bond distances, $\text{Mn}12$ of the synthetic compound has a different coordination sphere. The coordination number is seven with two $\text{O}25$ ($\equiv \text{H}_2\text{O}$) ligands instead of one of each $\text{O}1$, $\text{O}4$ and $\text{O}8$ (Fig. 5a and 5b).

Araki & Moore (1981) have already demonstrated that the complex structure type can be taken apart very conveniently into sheets parallel (0001) (Fig. 5–7), where only one fourth of the unit cell must be considered, because of the repeating unit along the c -axis. The most interesting level for our purpose is the slab at $z \sim 0$ containing the $(\text{Na}12)\text{O}_8$ - and $(\text{Mn}12)(\text{H}_2\text{O})_2\text{O}_3$ -polyhedra (Fig. 5a and 5b). It can be easily recognized that not a simple isostructural substitution is developed with slightly different coordination numbers, but both $\text{Na}12$ as well as $\text{Mn}12$ appear in its individual structural arrangement. The sheet with $\text{Na}12$ (Fig. 5a) is, as already mentioned, structurally almost similar with to fillowite. The coordination polyhedra of $(\text{Na}12)\text{O}_8$, named “gable disphe-noid” by Araki & Moore (1981), form six-member rings through common $\text{O}1$ around central $(\text{Mn}1)\text{O}_6$ octahedra (trigonal antiprism). The corresponding structural feature of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$ is remarkably different in

the case of Mn12 (Fig. 5b). The coordination polyhedron of $(\text{Mn}12)(\text{H}_2\text{O})_2\text{O}_5$ is strongly distorted. It can be described as a face-centered octahedron or as an octahedron with one divided vertex occupied by O1 and O22. The $(\text{Mn}12)(\text{H}_2\text{O})_2\text{O}_5$ polyhedra form six-member rings too. They are, however, linked together by $\text{H}_2\text{O}25$ and not by O1. This ring-type requires additional structural modifications concerning the surrounding polyhedra, where those of the $(\text{P}1)\text{O}_4$ tetrahedra are most easily recognized (Fig. 5a and 5b). Such strong structural differences most probably exclude simple isomorphous site by site substitution of Na12 and Mn12 on *M12*. It is more likely that whole six-member rings either of $(\text{Na}12)\text{O}_8$ - or of $(\text{Mn}12)(\text{H}_2\text{O})_2\text{O}_5$ -polyhedra replace each other, where no indication for ordering, e.g. sheet by sheet, has been observed during the single crystal study.

Bond-valence calculations

Bond-valence calculations according to $v_{ij} = \exp\{R_{ij} - d_{ij}/0.37\}$ [v.s.] (= valence units) were performed with the empirical values of Brown & Altermatt (1985) and gave either expected results for most of both the anions and cations are useful arguments in the case of uncertain coordination numbers, as already discussed above. It should be especially emphasized that the substitution of Na12 by Mn12 is in accordance with the bond-valence calculation results. The oxygens O24, O3 and a few others are unsaturated. But according to bond distances, given in the next chapter, the differences of O24 and O3 will be equilibrated by hydrogen bonds. The cation Mn4 appears probably strongly overbonded due to Mn^{3+} that is necessary, as mentioned above, for a charge-balanced chemical formula. A surprisingly low value of Mn12 is not the result of missing ligands, but originates probably from too long bond distances caused by interference with the Na12-O bonds, which could not be fully abolished by the structure refinement procedure.

The role of water in the fillowite structure

For Palache *et al.* (1951), fillowite contains essential water content, which is necessary to obtain a better correspondence between the calculated and measured densities. This hypothesis is not confirmed by Fisher (1965), who underlines the poor quality of the chemical analysis given by Palache *et al.* (1951), in which a large deficit of phosphorous occurs. Wet chemical analyses, realized on fillowite-type phosphates by Brush & Dana (1879, 1890), von Knorring (1963), Araki & Moore (1981), and Fransolet *et al.* (1998), reported however water contents between 0.55 and 1.66 wt. % H_2O . The role of water in fillowite-type phosphates is not discussed by Fransolet *et al.* (1998), probably because impurities can be responsible for the water content measured on some samples and minerals of the fillowite group are actually considered to be anhydrous (Gaines *et al.*, 1997; Strunz & Nickel, 2001).

The occurrence of a supplementary oxygen position, O25, in the synthetic fillowite-type phosphate investigated herein, indicates that water can play an essential role in the

fillowite structure-type. Besides this structural argument, it was thus of interest to confirm the presence of water by infrared spectroscopy. The infrared spectrum of the title compound, given in Figure 1, shows stretching vibrational modes of the PO_4 tetrahedra in the 1200–850 cm^{-1} region, as well as PO_4 bending vibrational modes between ca. 400 and 650 cm^{-1} . Two sharp bands at 3544 and 3527 cm^{-1} can be assigned to the stretching vibrational modes of molecular water, and the broad band at 1561 cm^{-1} to its bending mode, thus confirming that O25 corresponds to water. Starting from the bands at 3544 and 3527 cm^{-1} , and using the correlation proposed by Libowitzky (1999), it is possible to calculate the O-O distance between the two oxygens involved in the hydrogen bonds affecting the water molecule. These calculated O-O distances, of 2.98 and 2.94 Å fit with O25-O24 (2.87 Å) and O25-O3 (2.92 Å) distances of bended hydrogen bonds $\text{O}3 \cdots \text{H} - \text{O}25 - \text{H} \cdots \text{O}24$.

According to the site occupancy factors (Table 2), the amount of water in the title compound is 0.48 H_2O per formula unit, thus corresponding to only 0.14 wt. % H_2O . This very low amount, well below the amount measured in some natural samples that can reach 1.66 wt. % (Brush & Dana, 1879), has been detected by a single-crystal structure refinement and confirmed by infrared spectroscopy. It is thus necessary to investigate some natural fillowite samples with the same combined techniques, in order to shed some light on the role of water in this complex structure-type.

Conclusions

The structure-type of fillowite appears once more to be of large flexibility. Isomorphous or coupled substitution is detected in the crystal structure of $\text{Na}(\text{Na},\text{Mn})_7\text{Mn}_{22}(\text{PO}_4)_{18} \cdot 0.5\text{H}_2\text{O}$, compared with fillowite (Araki & Moore, 1981) and $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$ (Domanskii *et al.*, 1982), not only for atoms of different size and oxidation state on the same site, but also for clusters like the six-member rings of $(\text{Na}^+)\text{O}_8$ by $(\text{Mn}^{2+})(\text{H}_2\text{O})_2\text{O}_5$. We suppose that the large tolerance of this structure type results from its rod-packing, following Moore (1981, 1989), who has already described this feature that is relatively common for excitingly large and complex structures. He also draws attention to “ordered (cation) vacancies” (\square) that cut the rods into “stalks” and to their significance for the enormous complexity, e.g. fillowite, whose underlying principles are based on relative simplicity, e.g. α -Fe in multiple hexagonal setting (Moore, 1989). We have added further “ordered vacancies” to Rod I and III, although of unusual coordination sphere, but not excluded as cation positions according our experiences.

With respect to our results in this paper and ongoing investigations on other synthetic compounds and some minerals of the fillowite-type we assume that Rod I, composed of face-sharing polyhedra, provides the more stable “pillar” of the structural framework. Only site *M1* provides a second coordination sphere $\text{M1-O} \sim 2.85$ Å (for the synthetic compound), which would be suitable for Na^+ or Ca^{2+} . On the other hand, Rod II with its edge- and corner-sharing polyhedra and empty cation-position, as well as, Rod III with its partly empty cation-positions enable a variety of cation sites

variable with respect to size and coordination-spheres as well as the oxidation-state of the involved cations. The ambiguous coordination numbers discussed by Araki & Moore (1981) and in this paper for the cations on M6, M7, M10 and M11 all belong to Rod III. The most exciting example, as discussed above, is Na^+ and Mn^{2+} on site *M12* of Rod II.

Further attention should also be given to site $\text{O25} \equiv \text{H}_2\text{O}$ as well as to the “ordered vacancies” e.g. of Rod I and if possible structurally and analytically proved water content of other synthetic compounds and minerals should be determined.

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References

- Antenucci, D., Tarte, P., Fransolet, A.-M. (1996): The synthetic phosphate $\text{NaCaCdMg}_2(\text{PO}_4)_3$: first experimental evidence of a reversible alluaudite-fillowite polymorphism. *N. Jb. Miner. Mh.*, **1996**(7), 289–296.
- Araki, T. & Moore, P.B. (1981): Fallowite, $\text{Na}_2\text{Ca}(\text{Mn}, \text{Fe})^{2+}_7(\text{PO}_4)_6$; its crystal structure. *Am. Mineral.*, **66**, 827–842.
- Brown, I.D. & Altermatt, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Cryst.*, **B41**, 244–247.
- Brush, G.J. & Dana, E.S. (1878): On a new and remarkable mineral locality in Fairfield County, Connecticut; with description of several new species occurring there. *Am. J. Sci.*, **16**, 33–46.
- _____, _____ (1890): On the mineral locality at Branchville, Connecticut. With analyses of several manganese phosphates by H. L. Wells. *Am. J. Sci.*, **39**, 201–216.
- Domanskii, A.I., Smolin, Y.I., Shepelev, Y.F., Majling, J. (1982): Determination of crystal structure of triple magnesium calcium sodium orthophosphate $\text{Mg}_{21}\text{Ca}_4\text{Na}_4(\text{PO}_4)_{18}$. *Sov. Phys. Crystallogr.*, **27**(5), 535–537.
- Fisher, D.J. (1965): Dickinsonites, fillowite and alluaudites. *Am. Mineral.*, **50**, 1647–1669.
- Fransolet, A.-M. (1975): Etude minéralogique et pétrologique des phosphates de pegmatites granitiques. Unpublished Ph. D. Thesis, University of Liège, 333 p.
- Fransolet, A.-M., Fontan, F., Keller, P., Antenucci, D. (1998): La série johnsomervilleite-fillowite dans les associations de phosphates de pegmatites granitiques de l’Afrique centrale. *Can. Mineral.*, **36**, 355–366.
- Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. (1997): Dana’s new mineralogy, Eight edition. John Wiley & sons, New York, 1819 p.
- Hatert, F. (2002): Cristallographie et synthèse hydrothermale d’alluaudites dans le système Na-Mn-Fe-P-O: contribution au problème de la genèse de ces phosphates dans les pegmatites granitiques. Unpublished Ph. D. Thesis, University of Liège, 247 p.
- _____, _____ (2004): Etude cristallographie et synthèse hydrothermale des alluaudites. Une contribution nouvelle au problème génétique des phosphates de fer et de manganèse dans les pegmatites granitiques et, partant, à celui de l’évolution de ces gisements. *Acad. Roy. Belgique, Mém. Cl. Sci., in-8°, 3^e série*, **21**, 96 p.
- Hatert, F. & Fransolet, A.-M. (2003): Preliminary data on the crystal chemistry of synthetic fillowite-type phosphates. *Berichte der Deutschen Mineralogischen Gesellschaft, Beih. z. Eur. J. Mineral.*, **15**(1), 76.
- Herrendorf, W. & Bärmighausen, H. (1997): Numerical absorption correction with the help of the X-SHAPE software (Version 1.02) by STOE, Darmstadt, 1997, based on the program HABITUS.
- Keller, P. & Hess, H. (1988): Die Kristallstrukturen von O’Danielit, $\text{Na}(\text{Zn}, \text{Mg})_3\text{H}_2(\text{AsO}_4)_3$, und Johillerit, $\text{Na}(\text{Mg}, \text{Zn})_3\text{Cu}(\text{AsO}_4)_3$. – *N. Jb. Mineral. Mh.*, **1988**, 395–404.
- Keller, P., Riffel, N., Zettler, F. & Hess, H. (1981): $\text{AgCo}_3\text{H}_2(\text{AsO}_4)_3$ und $\text{AgZn}_3\text{H}_2(\text{AsO}_4)_3$. Darstellung und Kristallstruktur. Ein weiterer neuer Arsenat-Strukturtyp. *Z. anorg. allg. Chemie*, **474**, 123–134.
- Keller, P., Lissner, F., Hartert, F. & Schleid, Th. (2001): $\text{Na}_4(\text{Na}, \text{Mn})_4\text{Mn}_{22}(\text{PO}_4)_{18}$, eine isotype Verbindung der Fallowit-Johnsomervilleite-Reihe. *Z. Kristallogr., Suppl. Issue*, **18**, 150.
- Knorring, O. von (1963): VI(c) Report on mineralogical research. 7th Annual Report (1961–1962), Research Institute of African Geology, University of Leeds, 33–37.
- Libowitzky, E. (1999): Correlation of O-H stretching frequencies and O-H...O hydrogen bonds lengths in minerals. *Monat. Chem.*, **130**, 1047–1059.
- Livingstone, A. (1980): Johnsomervilleite, a new transition-metal phosphate mineral from the Loch Quoich area, Scotland. *Mineral. Mag.*, **43**, 833–836.
- McCoy, T.J., Steele, I.M., Keil, K., Leonard, B.F., Endreß, M. (1994): Chladniite, $\text{Na}_2\text{CaMg}_7(\text{PO}_4)_6$: A new mineral from the Carlton (IIICD) iron meteorite. *Am. Mineral.*, **79**, 375–380.
- Moore, P.B. (1981): Complex crystal structures related to glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$: evidence for very dense packings among oxysalts. *Bull. Minéral.*, **104**, 536–547.
- _____, _____ (1989): Perception of structural complexity: Fallowite revisited and α -iron related. *Am. Mineral.*, **74**, 918–926.
- Olsen, E.J. & Steele, I.M. (1997): Galileite: A new meteoritic phosphate mineral. *Meteoritics Planet. Sci.*, **32**, A155–A156.
- O’Neill, H.S.C. & Pownceby, M.I. (1993): Thermodynamic data from redox reactions at high temperatures. I. An experimental and theoretical assessment of the electrochemical method using stabilized zirconia electrolytes, with revised values for the Fe-“FeO”, Co-CoO, Ni-NiO and Cu-Cu₂O oxygen buffers, and new data for the W-WO₂ buffer. *Contrib. Mineral. Petrol.*, **114**, 296–314.
- Palache, C., Berman, H., Frondel, C. (1951): The system of Mineralogy, Vol. 2, 7th Ed., John Wiley & Sons, New York, pp. 719–720.
- Riffel, H., Keller, P. & Hess, H. (1985): Die Kristallstruktur von $\text{AgCu}_3\text{Cu}(\text{AsO}_4)_3$ und ihre strukturellen Beziehungen zu $\text{AgCo}_3\text{H}_2(\text{AsO}_4)_3$ bzw. $\text{AgZn}_3\text{H}_2(\text{AsO}_4)_3$. – *Z. anorg. allg. Chemie*, **530**, 60–68.
- Sheldrick, G.M. (1996): SHELXTL (1996). Version 5, Siemens Analytical Instruments Inc., Madison, WI, USA.
- _____, _____ (1997): SHELXL-97, Univ. Göttingen, Germany.
- Strunz, H. & Nickel, E.H. (2001): Strunz Mineralogical Tables, 9th edition. E. Schweizerbart’sche Verlagsbuchhandlung, Stuttgart, 870 p.
- Tuttle, O.F. (1949): Two pressure vessels for silicate-water studies. *Bull. Geol. Soc. Am.*, **60**, 1727–1729.

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