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THE CRYSTAL STRUCTURE OF BAKHCHISARAITSEVITE, $[Na_2(H_2O)_2]$ $\{(Mg_{4.5}Fe_{0.5})(PO_4)_4(H_2O)_5\}$, A NEW MINERAL SPECIES OF HYDROTHERMAL ORIGIN FROM THE KOVDOR PHOSCORITE–CARBONATITE COMPLEX, RUSSIA

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ABSTRACT

The crystal structure of a new mineral species, bakhchisaraitsevite $[Na_2(H_2O)_2]\{(Mg,Fe)_5(H_2O)_5(PO_4)_4\}$, a 8.3086(8), b 12.906(1), c 17.486(2) Å, β 102.01(1)°, V 1834.0(1) Å^3, space group $P2_1/c$, $Z = 4$, $\rho_{calc} = 2.499$ g/cm^3, has been determined [automated single-crystal diffractometer, Mo$K\alpha$, graphite monochromator, T = 193 K, 21597 reflections, $R = 0.033$ for 3527 unique reflections with $I \geq 2\sigma(I)$, $wR_2 = 0.072$]. It can be described as an open framework of Mg(Fe) octahedra and PO_4 tetrahedra. Extremely contorted chains of edge-sharing Mg(Fe) octahedra form layers parallel to the ***ab*** plane. The unit cell of bakhchisaraitsevite contains two layers of this kind. In the ***c*** direction, these layers are also joined by dimers of Mg(Fe) octahedra having common edges. The PO_4 tetrahedra consolidate the structure, sharing the majority of vertices with octahedra. Na atoms and H_2O molecules are distributed in the channels of an open framework. The main feature of the crystal structure, layers of octahedra parallel to the ***ab*** plane, explains the flattened habit and the perfect cleavage of the crystals. The crystal-chemical formula of the mineral, $[Na_2(H_2O)_2]\{(Mg_{4.5}Fe_{0.5})(H_2O)_5(PO_4)_4\}$, where curly brackets enclose the framework component and square brackets show the contents of the channels, reflects the different functions of the H_2O molecules in the structure. Bakhchisaraitsevite as a possible biomineral can be expected to play a role in accumulating phosphorus in recent sulfidic sediments with the participation of bacteria. We describe the close structural relations between bakhchisaraitsevite and rimkorolgite.

Keywords: bakhchisaraitsevite, rimkorolgite, crystal structure, refinement.

SOMMAIRE

Nous avons affiné la structure cristalline de la nouvelle espèce minérale bakhchisaraïtsévite, $[Na_2(H_2O)_2]\{(Mg,Fe)_5(H_2O)_5(PO_4)_4\}$, a 8.3086(8), b 12.906(1), c 17.486(2) Å, β 102.01(1)°, V 1834.0(1) Å^3, groupe spatial $P2_1/c$, $Z = 4$, $\rho_{calc} = 2.499$ g/cm^3 [diffractomètre à cristal unique automatisé, rayonnement Mo$K\alpha$, monochromatisation au graphite, T = 193 K, 21597 réflexions, $R = 0.033$ pour 3527 réflexions uniques pour lesquelles $I \geq 2\sigma(I)$, $wR_2 = 0.072$]. On peut considérer cette structure en termes d'une trame ouverte d'octaèdres Mg(Fe) et de tétraèdres PO_4. Des chaînes extrêmement difformes de tels octaèdres à arêtes partagées définissent des couches parallèles au plan ***ab***. La maille élémentaire de la bakhchisaraïtsévite contient deux sortes de couches de ce type. Le long de ***c***, ces couches sont rattachées par des dimères d'octaèdres Mg(Fe) partageant aussi leurs arêtes. Les tétraèdres PO_4 assurent la consolidation de la structure en partageant la plupart de leurs coins avec les octaèdres. Les atomes Na et les molécules de H_2O logent dans les canaux de la trame ouverte. Le module principal de la structure, les couches d'octaèdres parallèles au plan ***ab***, rend compte de la forme applatie et du clivage parfait des cristaux. La formule cristallochimique de la

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bakhchisaraïtsévite, $[Na_2(H_2O)_2]\{(Mg_{4.5}Fe_{0.5})(H_2O)_5(PO_4)_4\}$, où les accolades renferment les composants de la trame, et les crochets, ceux des canaux, exprime les différentes fonctions des molécules de H_2O dans la structure. La bakhchisaraïtsévite pourrait bien être importante dans l'accumulation de phosphore dans des sédiments sulfurés récents grâce à la participation de bactéries. Nous traitons des relations structurales étroites entre bakhchisaraïtsévite et rimkorolgite.

(Traduit par la Rédaction)

Mots-clés: bakhchisaraïtsévite, rimkorolgite, structure cristalline, affinement.

INTRODUCTION

Recently, Liferovich *et al.* (in press) described a hydrated sodium and magnesium phosphate mineral, bakhchisaraitsevite, as a new mineral species. It was discovered in assemblages of hydrothermal minerals related to vuggy veins of dolomite carbonatite of the Kovdor alkaline-ultrabasic massif, Kola alkaline province, northwestern Russia. Hydrothermal activity followed the postmagmatic tectonic events superimposed on the latest dolomite veins. Hydrothermal minerals are confined to fissures and epigenetic cavities formed in massive dolomite carbonatite owing to the alteration of primary sulfides by low-temperature solutions. Assemblages in voids contain many rare phosphates, among them hydrous phosphates of Mg: kovdorskite, bonshtedtite, girvasite, strontiowhitlockite, rimkorolgite, krasnovite, juonniite, and gladiusite (recently approved by the IMA CNMMN); more common are collinsite, baričite and bobierrite. The variety and abundance of rare magnesium phosphate species are notable features of epigenetic mineral assemblages related to carbonatite of the Kovdor massif.

Bakhchisaraitsevite occurs in cavities as free-standing fan-shaped aggregates with perfect cleavage or as flattened crystals of 0.5 × 1.5 × 4 mm (Fig. 1) and hence amenable to crystal-structure analysis.

The mineral species was identified as "new" by determination of the chemical composition, unit cell (which did not correspond to any known sodium phosphates) and solution and refinement of crystal structure; the results are presented here. Both the new mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA (#99–005).

CHEMICAL COMPOSITION

Bakhchisaraitsevite crystals were analyzed with a Cameca MS–46 electron microprobe. Each composition was taken into account; the data were averaged out of 3 or 4 local measurements in adjacent points of a bakhchisaraitsevite crystal; the samples were moved during analyses to minimize decomposition under the electron beam. The conditions were optimized with an accelerating potential of 20 kV and sample current of 30 nA. The following standards were used: lorenzenite (Na), pyrope (Mg), apatite (Ca and P), synthetic $MnCO_3$ (Mn), hematite (Fe), barite (Ba) and celestine (Sr). The crystals are practically homogeneous in terms of distribution of the main cations. A representative composition of the crystal studied is given in Table 1. The infrared spectrum indicates the presence of phosphate groups and H_2O molecules; no other anionic groups were found (the absence of F and CO_2 was confirmed by wet microchemical analysis, O.G. Lekhanova, analyst (GI KSC RAS). Thus the shortfall in the analytical totals was assumed to reflect the H_2O content.

FIG. 1. Crystals of bakhchisaraitsevite in hydrothermal assemblage with colorless bobierrite on dolomite from a cavity in a deformed vein of dolomite carbonatite. Photographed by Nataly A. Pekova, Fersman Mineralogical Museum, Moscow, Russia.

TABLE 1. CHEMICAL COMPOSITION OF BAKHCHISARAITSEVITE

Constituent	Range	Standard deviation	Representative composition	Idealized composition
Na_2O wt%	7.62–9.21	0.4	8.48	9.20
MgO	25.40–30.88	0.4	26.73	29.94
CaO	0–0.12	0.02	0.05	-
MnO	0.25–1.81	0.02	0.78	-
FeO	0.82–5.80	0.02	5.26	-
H_2O *			18.17	18.72
P_2O_5	40.28–42.47	0.4	40.91	42.14
Total			100.38	100.0

* calculated assuming seven molecules of H_2O. The idealized composition corresponds to the formula $Na_2Mg_5(PO_4)_4(H_2O)_7$.

The empirical formula of the new phosphate mineral, calculated on the basis of structure data indicating four atoms of P and seven H_2O groups per unit cell, is $(Na_{1.90}Ca_{0.01})_{\Sigma 1.91}(Mg_{4.54}Fe^{2+}_{0.51}Mn_{0.08})_{\Sigma 5.13}P_4O_{16.09}(H_2O)_7$ or, ideally, $Na_2(Mg,Fe)_5(PO_4)_4(H_2O)_7$.

STRUCTURE DETERMINATION

The unit-cell parameters of bakhchisaraitsevite (monoclinic) were obtained using a SYNTEX P1 four-circle single-crystal diffractometer (T = 273 K): *a* 8.324(4), *b* 12.926(4), *c* 17.519(9) Å, β 102.03°(1), *V* = 1844 Å^3. Because of the significant contents of H_2O in the formula, we also collected structural data under low-temperature conditions (T = 193 K) using an IPDS area-detector system (Stoe 1997) with Mo*K*α radiation (graphite monochromator). The intensities were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction was applied using equivalent reflections. In Table 2, we report the crystallographic characteristics of bakhchisaraitsevite and the experimental conditions of data collection and refinement.

TABLE 2. CRYSTAL DATA AND DETAILS OF THE X-RAY DATA COLLECTION AND REFINEMENT FOR BAKHCHISARAITSEVITE

Crystal data			
a (Å)	8.3086(8)	Formula	$Na_2(H_2O)_2\{(Mg,Fe)_5(H_2O)_5[PO_4]_4\}$
b (Å)	12.906(1)	*Z*	4
c (Å)	17.486(2)		
β (°)	102.01(1)	Density $D_{calc.}$ (g/cm^3)	2.499
V (Å^3)	1834.0(1)	Absorption coef. μ (mm^{-1})	1.13
Space group	$P2_1/c$		
Data collection			
Crystal size (mm)	0.05×0.08×0.1	$-11 \le h \le 11, -17 \le k \le 17, -24 \le l \le 24$	
Diffractometer	IPDS (Stoe)	Reflections (total)	21597
Monochromator	graphite	R_σ	0.070
Radiation	Mo*K*α	$R_{int.}$	0.067
Range $(2\theta)_{max}$	61°	*T*	193 K
Recording mode	Φ = 0–200°, δΦ = 1°, 3min/rec		
Refinement			
Reflections (unique)	5397	Number of parameters	369
[observed with $I \ge 2\sigma(I)$]	3527		
R (observed)	0.033	Extinction coefficient	0.0006(2)
S	0.863	δρ (max)	0.55 *e*/Å^3
wR_2 (all F^2)	0.072	δρ (min)	−0.65 *e*/Å^3

All calculations were performed with the SHELX package of programs (Sheldrick 1997a, b). Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography (Hahn 1995). The structure of the new mineral was solved in the space group $P2_1/c$ by direct methods and was refined using the F^2 data to residuals $wR_2 = 0.072$ (for all reflections) and $R = 0.033$ [for 3527 reflections with $I \ge 2\sigma(I)$] with anisotropic displacement parameters for all non-H atoms.

Refinements of site occupancies show that the very small amount of Fe^{2+} cations in the structure of bakhchisaraitsevite is distributed over all five independent *M* positions, which are mainly occupied by Mg atoms. During the refinement, the temperature parameters of Mg and Fe were constrained to be equal. The following site-occupancies were determined: *M*1 [0.767(3) Mg + 0.233 Fe], *M*2 [0.883(3) Mg + 0.117 Fe], *M*3 [0.910(3) Mg + 0.090 Fe], *M*4 [0.943(3) Mg + 0.057 Fe], *M*5 [0.969(3) Mg + 0.031 Fe].

The oxygen atoms of H_2O molecules in eight independent positions were identified on the basis of a bond-valence analysis. The positions of 16 independent H atoms were obtained from difference-Fourier syntheses and were refined under isotropic approximation. During the last step of the refinement, identical values of the isotropic temperature-parameters were assigned to those H atoms belonging to the same H_2O molecule. In order to obtain adequate geometrical characteristics for hydrogen bonds, the distances *D* – H were restricted to a fixed value of 0.85 Å (Sheldrick 1997b). The atomic coordinates and interatomic distances obtained are given in Tables 3 and 4. Table 5 presents the geometrical characteristics of hydrogen bonds. The results of the bond-valence analysis (Pyatenko 1972, Brown 1976) are given in Table 6.

INTERATOMIC DISTANCES

Four vertices of each of four independent octahedra (*M*2–*M*5) are occupied by the O atoms of phosphate groups (henceforth O_P), and two vertices, by O atoms of H_2O molecules (henceforth O_W). The interatomic distances in these polyhedra M–O_W vary from 2.118 to 2.320 Å and are normally larger than those of M–O_P, which are in the range of 1.989–2.104 Å. Five O_P and one O_W form the coordination polyhedron of the fifth independent Mg(Fe) atom in the *M*1 position. In that polyhedron, the interatomic distance $M1$–O_{W5} = 2.124 Å is not the largest: distances *M*1–O vary from 2.067 to 2.256 Å. An analysis of averaged distances *M*–O in *M*-octahedra (Table 4) shows that a smaller proportion of

Fe^{2+} cations [r(^{VI}Fe) = 0.78 Å], which are larger than Mg^{2+} [r(^{VI}Mg) = 0.72 Å] (Shannon 1976), corresponds normally to a smaller average "cation–oxygen" distance in a polyhedron. Thus, the increase of Fe atom contents in octahedra from 3% (*M*5) to 23% (*M*1) is accompanied by an increase of the average *M*–O distance from 2.076 to 2.127 Å.

The two independent Na^+ cations are placed in a seven-vertex polyhedron (Na1) and a five-vertex polyhedron (Na2). Oxygen atoms of the H_2O molecules are found in both polyhedron surroundings. In the case of Na1, positionally disordered O_{W7a} and O_{W7b} of H_2O

TABLE 3. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR BAKHCHISARAITSEVITE

Atom	*x*	*y*	*z*	*U*eq
Mg1	–0.13637(7)	–0.07430(7)	0.44872(5)	0.0067(2)
Mg2	0.21678(8)	–0.08847(8)	0.26602(6)	0.0062(2)
Mg3	0.31471(8)	0.17700(8)	0.26855(6)	0.0060(3)
Mg4	0.30351(8)	–0.31843(8)	0.25206(6)	0.0054(3)
Mg5	–0.18402(9)	–0.09404(9)	0.24526(7)	0.0058(3)
P1	0.04373(7)	0.07984(7)	0.35341(5)	0.0049(1)
P2	0.03566(7)	–0.25540(7)	0.35853(5)	0.0051(1)
P3	0.55106(7)	0.34764(7)	0.36123(5)	0.0079(1)
P4	–0.42473(7)	0.00711(7)	0.35771(5)	0.0066(1)
Na1	0.16505(14)	0.70359(14)	0.05837(11)	0.0221(3)
Na2	–0.40446(18)	0.14046(18)	0.53562(12)	0.0304(3)
O1	0.02926(21)	–0.18673(15)	0.42911(10)	0.0102(4)
O2	–0.34867(22)	0.03660(15)	0.44224(10)	0.0131(4)
O3	0.02394(19)	0.04749(14)	0.43601(9)	0.0074(3)
O4	–0.28976(20)	–0.06189(15)	0.33479(9)	0.0103(4)
O5	0.55835(21)	0.46566(15)	0.37550(10)	0.0108(4)
O6	0.02633(19)	–0.01600(14)	0.30043(9)	0.0068(3)
O7	0.18998(19)	–0.22723(15)	0.32508(9)	0.0076(3)
O8	0.59606(22)	0.29045(16)	0.43881(10)	0.0142(4)
O9	0.67195(20)	0.32070(14)	0.30722(10)	0.0085(3)
O10	0.04596(20)	–0.37083(14)	0.38160(10)	0.0084(3)
O11	–0.58065(20)	–0.05757(16)	0.34911(10)	0.0126(4)
O12	–0.45943(19)	0.10304(14)	0.30425(10)	0.0078(3)
O13	–0.11993(19)	–0.23818(14)	0.29423(9)	0.0075(3)
O14	0.37649(19)	0.31992(14)	0.31694(9)	0.0077(3)
O15	–0.09132(19)	0.15944(14)	0.32326(9)	0.0075(3)
O16	0.21202(20)	0.13008(15)	0.35773(10)	0.0083(3)
O_{W1}	0.23229(20)	0.04585(14)	0.19733(10)	0.0079(3)
H1	0.295(3)	0.025(3)	0.168(1)	0.028(7)
H2	0.141(2)	0.066(6)	0.170(2)	0.028(7)
O_{W2}	–0.01579(21)	–0.13758(15)	0.17512(10)	0.0093(3)
H3	0.012(4)	–0.203(2)	0.178(2)	0.026(7)
H4	–0.023(4)	–0.116(3)	0.129(1)	0.026(7)
O_{W3}	0.45950(21)	0.22384(16)	0.17696(10)	0.0099(3)
H5	0.450(5)	0.193(3)	0.133(1)	0.036(8)
H6	0.444(5)	0.288(1)	0.169(2)	0.036(8)
O_{W4}	0.26955(20)	–0.45535(15)	0.31726(10)	0.0081(3)
H7	0.206(3)	–0.428(3)	0.344(2)	0.037(8)
H8	0.361(2)	–0.480(3)	0.341(2)	0.037(8)
O_{W5}	0.29515(25)	0.17696(17)	0.50720(11)	0.0164(4)
H9	0.300(5)	0.242(1)	0.512(2)	0.041(8)
H10	0.288(5)	0.167(3)	0.458(1)	0.041(8)
O_{W6}	0.58900(32)	0.62982(20)	0.46553(13)	0.0268(5)
H11	0.524(4)	0.651(4)	0.494(2)	0.059(12)
H12	0.568(11)	0.568(3)	0.449(5)	0.059(12)
H13	0.665(8)	0.600(7)	0.498(4)	0.059(12)
O_{W7a}	–0.0410(7)	0.8835(5)	0.0259(3)	0.0286(8)
H14	0.018(6)	0.887(4)	–0.012(3)	0.069(13)
O_{W7b}	0.0697(5)	0.8956(4)	0.0370(2)	0.0286(8)
H15*	–0.139(5)	0.903(9)	0.008(6)	0.069(13)
H16**	0.167(4)	0.920(7)	0.047(5)	0.069(13)

* *G* = 0.429; ** *G* = 0.571.

TABLE 4. BOND LENGTHS (Å) IN BAKHCHISARAITSEVITE

Mg1 octahedron			Mg2 octahedron			Mg3 octahedron		
Mg1 –	O3	2.067(2)	Mg2 –	O11	2.021(2)	Mg3 –	O16	2.020(2)
	O1	2.077(2)		O6	2.034(2)		O14	2.050(2)
	O3	2.102(2)		O9	2.088(2)		O13	2.070(2)
	O_{W5}	2.124(2)		O7	2.102(2)		O12	2.082(2)
	O4	2.136(2)		O_{W1}	2.128(2)		O_{W1}	2.128(2)
	O2	2.256(2)		O_{W2}	2.320(2)		O_{W3}	2.276(2)
average		2.127	average		2.116	average		2.104
Mg4 octahedron			Mg5 octahedron			P1 tetrahedron		
Mg4 –	O15	1.989(2)	Mg5 –	O4	1.992(2)	P1 –	O16	1.529(2)
	O12	2.051(2)		O14	2.061(2)		O15	1.532(2)
	O7	2.099(2)		O13	2.071(2)		O6	1.534(2)
	O9	2.104(2)		O6	2.073(2)		O3	1.545(2)
	O_{W4}	2.153(2)		O_{W2}	2.118(2)	average		1.535
	O_{W3}	2.168(2)		O_{W4}	2.140(2)			
average		2.094	average		2.076			
P2 tetrahedron			P3 tetrahedron			P4 tetrahedron		
P2 –	O1	1.529(2)	P3 –	O8	1.521(2)	P4 –	O11	1.522(2)
	O10	1.541(2)		O14	1.538(2)		O2	1.530(2)
	O13	1.543(2)		O5	1.543(2)		O12	1.542(2)
	O7	1.559(2)		O9	1.554(2)		O4	1.549(2)
average		1.543	average		1.539	average		1.536
Na1 polyhedron			Na2 polyhedron					
Na1 –	O8	2.271(2)	Na2 –	O2	2.234(2)			
	O1	2.317(2)		O11	2.308(2)			
	O15	2.348(2)		O_{W5}	2.486(2)			
	O3	2.569(2)		O8	2.572(2)			
	O2	2.642(2)		O7	2.925(2)			
	O9	2.884(2)	average		2.505			
	O_{W7b}	2.605(5)						
	[O_{W7a}	2.871(6)]						
average		2.519 (2.557)						

TABLE 5. H-BONDING IN BAKHCHISARAITSEVITE
$(Na_2H_2O)(H_2O)\{(Mg_{4.5}Fe_{0.5})(H_2O)_4[PO_4]_4\}$

D – H ····· *A*			*D* – H, Å	H ····· *A*, Å	*D* ····· *A*, Å	angle, °
O_{W1}	–	H1 ··· O5	0.85(2)	1.74(2)	2.577(2)	168(3)
O_{W1}	–	H2 ··· O10	0.85(3)	1.82(3)	2.661(2)	171(4)
O_{W2}	–	H3 ··· O15	0.85(1)	1.97(1)	2.765(3)	155(3)
O_{W2}	–	H4 ··· O_{W7a}	0.85(2)	1.77(2)	2.589(4)	150(3)
		····· O_{W7b}	0.85(2)	1.92(2)	2.690(4)	160(3)
O_{W3}	–	H5 ··· O_{W6}	0.85(3)	1.88(2)	2.725(3)	174(4)
O_{W3}	–	H6 ··· O4	0.85(1)	2.31(2)	3.091(3)	153(4)
		····· O11	0.85(1)	2.34(2)	3.061(3)	142(4)
O_{W4}	–	H7 ··· O10	0.85(3)	1.76(3)	2.603(2)	168(3)
O_{W4}	–	H8 ··· O5	0.85(3)	1.77(3)	2.611(2)	171(3)
O_{W5}	–	H9 ··· O_{W6}	0.85(1)	1.89(2)	2.680(3)	154(4)
O_{W5}	–	H10 ··· O16	0.85(1)	1.81(1)	2.631(2)	162(4)
O_{W6}	–	H11 ··· O8	0.85(4)	1.85(4)	2.701(3)	173(4)
O_{W6}	–	H12 ··· O5	0.85(5)	1.83(4)	2.620(3)	153(8)
O_{W6}	–	H13 ··· O_{W7}	0.85(5)	2.40(4)	3.040(3)	133(8)
O_{W7a}	–	H14 ··· O10	0.90(5)	1.94(6)	2.770(4)	153(7)
O_{W7b}	–	H14 ··· O10	0.88(5)	1.94(6)	2.702(4)	145(7)
O_{W7a}	–	H15 ··· O_{W6}	0.85(5)	2.27(5)	3.041(3)	151(8)
O_{W7b}	–	H16 ··· O5	0.85(5)	2.47(6)	3.278(5)	158(8)
		····· O8	0.85(5)	2.56(7)	3.041(5)	117(7)

angle: *D* – H ····· *A*. *D*: donor, *A*: acceptor.

TABLE 6. BOND-VALENCE ANALYSIS FOR BAKHCHISARAITSEVITE

Cation Anion	*M*1	*M*2	*M*3	*M*4	*M*5	P1	P2	P3	P4	Na1	Na2	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	H12	H13	H14	H15	H16	Σ	δ
O1	0.363						1.328			0.173																		1.864	0.136
O2	0.267								1.281	0.125	0.256																	1.929	0.071
O3	0.342					1.206				0.135																		2.053	0.053
	0.370																												
O4	0.327				0.393				1.181								0.04											1.941	0.059
O5								1.224				0.32							0.29				0.14				0.01	1.993	0.007
O6		0.385			0.330	1.256																						1.971	0.029
O7		0.336		0.328			1.172				0.130																	1.966	0.034
O8								1.352		0.183	0.180											0.22					0.04	1.975	0.025
O9		0.343		0.321				1.173		0.101																		1.938	0.062
O10							1.250						0.26					0.30							0.20			2.010	0.010
O11		0.392							1.332		0.237						0.05											2.011	0.011
O12			0.339	0.361					1.206																			1.906	0.094
O13			0.353		0.336		1.250																					1.939	0.061
O14			0.366		0.343			1.250																				1.959	0.041
O15				0.407		1.256				0.167				0.19														2.020	0.020
O16			0.393			1.281															0.27							1.944	0.056
O_{W1}		0.322	0.312									0.68	0.74															2.054	0.054
O_{W2}		0.224			0.305									0.81	0.73													2.069	0.031
O_{W3}			0.237	0.289												0.79	0.91											2.226	0.226
O_{W4}				0.295	0.293													0.70	0.71									1.998	0.002
O_{W5}	0.334										0.197									0.76	0.73							2.021	0.021
O_{W6}																0.21				0.24		0.78	0.36	0.45		0.04		2.080	0.080
O_{W7a} (O_{W7b})										0.118					0.27									0.05	0.80	0.39	0.52	2.098	0.098
																												$\Sigma\delta = 1.281$	

$D = (1.281 : 46) \cdot 100\% = 2.8\%$

molecules at a separation of 0.913(7) Å occupy their positions in the structure with a probability of occupancy of 43% and 57%, correspondingly. This statistical mode of occurrence of the H_2O molecule in the cavities of zeolites and zeolite-like compounds is quite typical and was, for instance, described in the crystal structures of laumontite (Yakubovich & Simonov 1985) and merlinoite (Yakubovich *et al.* 1999). In the seven-vertex polyhedron occupied by Na1, the Na–O distances vary from 2.271 to 2.884 Å; the Na–O_W distance of 2.605 (2.871) Å is not the largest for this polyhedron, because O_{W7a} and O_{W7b} coordinate with Na1 atoms only. In the five-vertex Na2 polyhedron, four Na2–O bonds (2.234–2.572 Å including bond Na2–O_{W5} = 2.486 Å) form a tetrahedron. The fifth distance, Na2–O7 = 2.925 Å, is markedly longer than the average (2.505 Å) in the polyhedron.

The interatomic P–O distances in the four independent phosphate tetrahedra are within the range of 1.521 to 1.559 Å. Two remaining oxygen atoms, O5 and O10, are not directly bonded to other cations. The formal bond-valence sums to these oxygen atoms is 1.25 vu (valence units); this value confirms their role as acceptors of the majority of the hydrogen bonds in the crystal structure (Tables 5, 6).

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A microporous zeolite-like mixed framework of octahedra and tetrahedra is the basis of the crystal structure of bakhchisaraitsevite. Extremely contorted chains of edge-sharing Mg(Fe) octahedra are corner-linked to form perforated and somewhat corrugated layers parallel to the ***ab*** plane (Fig. 2). A unit cell of bakhchisaraitsevite contains two layers of this kind. In the ***c*** direction, these layers are also joined by edge-sharing dimers of Mg(Fe) octahedra (Fig. 3). The PO_4 tetrahedra consolidate the structure, sharing the majority of their vertices with octahedra. Na atoms and H_2O molecules are distributed in the channels of an open framework. The main feature of the crystal structure, layers of octahedra parallel to the ***ab*** plane, explains the flattened habit of bakhchisaraitsevite crystals and its perfect cleavage.

The eight independent H_2O molecules play different crystallochemical roles in the structure. Four of them, O_{W1} to O_{W4}, participate in the coordination of two *M*-octahedra. The O_{W5} oxygen atom is included in the first coordination sphere of one *M* octahedron and of the Na2 five-vertex polyhedron. Thus, five H_2O molecules participate in the framework of the structure. Two atoms O_{W7a} and O_{W7b} at a distance of 0.9 Å from each other occupy the structural positions statistically and coordinate the Na1 seven-vertex polyhedron. Like the Na atoms, they are non-framework components, located in channels of the three-dimensional framework of octahedra and tetrahedra. The H_2O molecule O_{W6} has a zeolitic character and does not participate in the coordination of any cation of the structure. The O_{W6}, O_{W7a} and O_{W7b} atoms play the role of hydrogen-bond acceptors

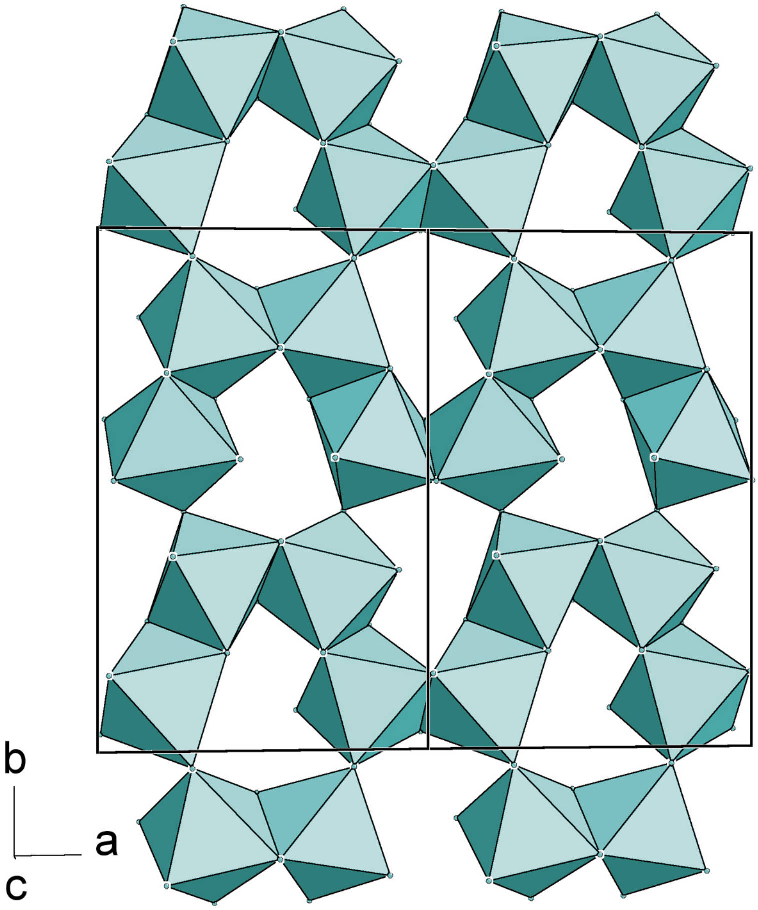

FIG. 2. Cellular layers of edge-sharing Mg(Fe) octahedra in crystal structure of bakhchisaraitsevite. View along the *c* axis. Circles represent Na, P atoms and O atoms of H_2O molecules.

(Table 5). The crystal-chemical formula of the mineral can be written as $[Na_2\ (H_2O)\ (H_2O)]\ \{(Mg_{4.5}\ Fe_{0.5})_{\Sigma 5}\ (PO_4)_4 \bullet (H_2O)_5\}$, where the curly brackets emphasize the framework components, and square brackets show the contents of the channels. This formula reflects the different functions of the H_2O molecules in the structure of bakhchisaraitsevite.

The system of the hydrogen bonds in the structure is quite complicated. Two weak hydrogen bonds of the bifurcated type, $O_{W3} – H6 \ldots O$ bonds are observed with donor–acceptor distances $O_{W3} \ldots O4 = 3.091(3)$ Å and $O_{W3} \ldots O11 = 3.061(3)$ Å. A similar pattern is observed for the hydrogen bonds $O_{W7b} – H16 \ldots O$, where the bifurcated configuration correlates with the greater donor–acceptor distances: $O_{W7b} \ldots O5 = 3.278(5)$ Å and $O_{W7b} \ldots O8 = 3.040(5)$ Å. The structural position of one of the H atoms of the zeolitic molecule of H_2O, O_{W6}, proves to be split in two equally probable atoms (H12 and H13) with corresponding hydrogen bonds $O_{W6} \ldots O5 = 2.620(3)$ Å and $O_{W6} \ldots O_{W7a} = 3.040(3)$ Å. Two disordered oxygen atoms, O_{W7a} and O_{W7b}, share one common H atom (H15), which fully occupies the corresponding structural position (Table 6, Fig. 4).

STRUCTURAL AND GENETIC RELATIONS

A similarity in unit-cell parameters and chemical formulae lead us to suspect a structural similarity between bakhchisaraitsevite and rimkorolgite $(Ba,Sr,Ca)(Mg, Mn)_5(PO_4)_4(H_2O)_8$ (Table 7). The crystal structure of rimkorolgite has not yet been studied, but the symmetry of this phosphate mineral from the same

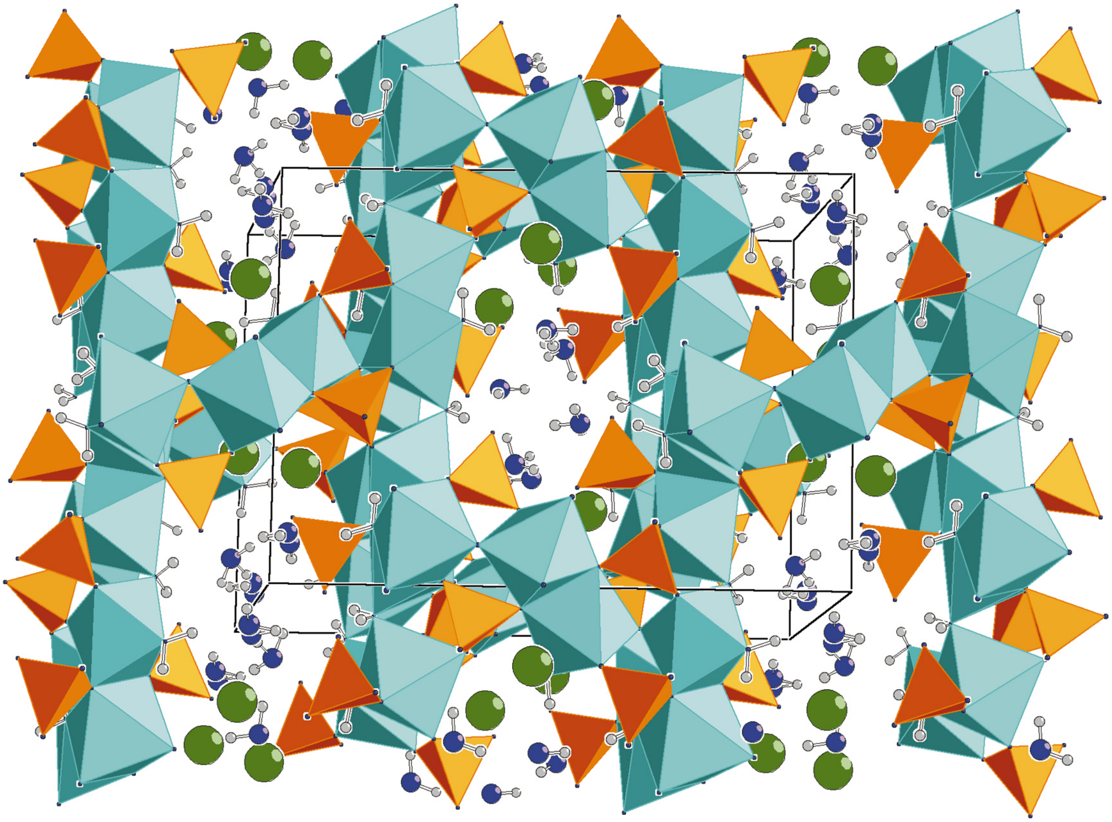

FIG. 3. Crystal structure of bakhchisaraitsevite projected onto the plane ***bc***. Large circles represent Na atoms, and small circles, O atoms of H_2O molecules.

TABLE 7. CRYSTAL DATA FOR COMPOUNDS RELATED TO BAKHCHISARAITSEVITE

	Unit-cell parameters, Å (°)		Space group	*Z*	D_{meas} g/cm^3
Rimkorolgite	*a*	8.335(2)			
$(Ba,Sr,Ca)(Mg,Mn)_5(PO_4)_4(H_2O)_8$	*b*	12.829(4)	*Pmcm* (?)	4	2.67
(Britvin *et al.* 1995)	*c*	18.312(3)			
Bakhchisaraitsevite	*a*	8.324(4)			
$Na_2(Mg,Fe)_5(PO_4)_4(H_2O)_7$	*b*	12.926(4)	$P2_1/c$	4	2.50
	c	17.519(9)			
	β	102.03(4)			
Synthetic phosphate	*a*	8.33			
$KNa_3(Mg,Fe)_4(PO_4)_3(OH)_3$ (?)	b	12.86	$P2_1/c$	4	2.13
(Hallberg & Wadsten 1980)	*c*	17.55			
	β	102.6			

hydrothermal assemblages of the Kovdor massif is presumed to be orthorhombic. Thin intergrowths of rimkorolgite crystals were described in the holotype material (Britvin *et al.* 1995). As can be seen in Table 7, in the case of bakhchisaraitsevite, as well as in case of rimkorolgite, the glide plane ***c*** is perpendicular to the 12.8 Å unit-cell axis; this suggests that rimkorolgite has monoclinic symmetry as well (orthorhombic pseudosymmetry may be the result of polysynthetic twinning of the crystals).

Hallberg & Wadsten (1980) reported on a new sodium phosphate mineral formed in the course of microbial experiments involving continuous cultivation of sulfate-reducing bacteria. Under current conditions of sedimentation, bacteria may act as a template in the formation of iron sulfide in the reaction between Fe and hydrogen sulfide excreted by bacteria. The experiments of Hallberg & Wadsten were made under controlled conditions as commensurate as possible with those in modern sediments. An unknown sodium phosphate, stable in air at pH ≈ 8 and up to T = 390 K, was ob-

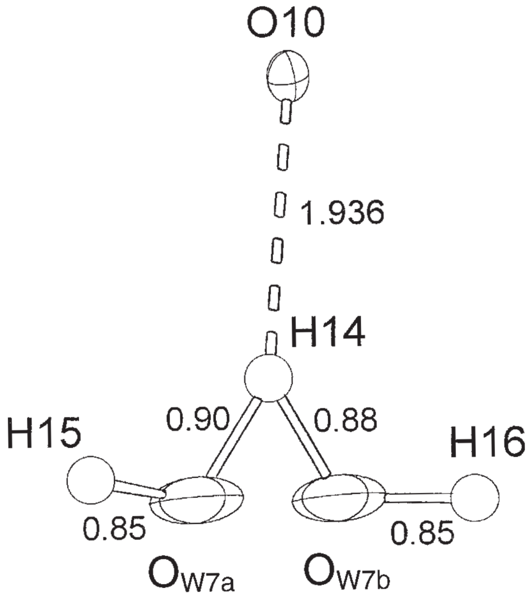

FIG. 4. Hydrogen bonding at the disordered O_{W7a}/O_{W7b} H_2O molecule.

tained (Table 7). At this temperature, the compound decomposes, probably owing to a loss of the H_2O. The symmetry, the unit-cell parameters and the formula (rather approximate) allow us to infer that the synthetic phase described by Hallberg & Wadsten (1980) is a K-rich variety of bakhchisaraitsevite. The authors mentioned that the new compound should be sought in nature, as it could be an important mineral for phosphate fixation in sediments. As it was formed only in the cultivation at pH ≈ 8, it could serve as a paleo-pH indicator in the sediment formation (Hallberg & Wadsten 1980), for example in recent sulfidic marine sediments as well as in sedimentary sulfide ores. In our case, bakhchisaraitsevite also was encountered in association with dissolved pyrrhotite in altered hydrothermal zones of deformed veins of dolomite carbonatite. The information available allows us to raise the possibility that bakhchisaraitsevite is a biogenic mineral, accumulating phosphorus in supergene processes with the participation of bacteria.

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