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THE CRYSTAL STRUCTURE OF BARIĆITE, $(Mg_{1.70}Fe_{1.30})(PO_4)_2\bullet 8H_2O$, THE MAGNESIUM-DOMINANT MEMBER OF THE VIVIANITE GROUP

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ABSTRACT

The crystal structure of barićite, the Mg-dominant analogue of vivianite, $(Mg_{1.70}Fe^{2+}_{1.30-x}Fe^{3+}_{x})(PO_4)_2(OH)_x\bullet(8-x)H_2O$, a 10.085(2), b 13.390(3), c 4.6713(9) Å, β 104.96(3)°, V 609.4(1) Å^3, space group $C2/m$, $Z = 2$, $\rho_{calc} = 2.440$ g/cm^3, has been determined [automated single-crystal diffractometer, Mo$K\alpha$, graphite monochromator, image-plate area-detector system, T = 193 K, 5714 reflections, $wR_2 = 0.106$ for all 1244 unique reflections, $R = 0.043$ for 965 observed reflections with $I \leq 2\sigma(I)$]. A refinement of site occupancies shows that Fe and Mg are partially ordered in the structure. According to X-ray and Mössbauer data, the position at the center of symmetry ($M1$) is mainly occupied by Fe, whereas Mg prefers the position at the two-fold axis ($M2$); Fe atoms occupy two-thirds of the $M1$ and one-third of $M2$ octahedra. The positions of four independent H atoms were obtained from difference-Fourier syntheses and were refined under isotropic approximation. The crystal structure of barićite consists of two type of octahedral structural units: isolated $M1O_2(H_2O)_4$ octahedra and clusters of two edge-sharing polyhedra $M2O_6(H_2O)_4$. These octahedral units are connected in the structure by orthophosphate tetrahedra to form layers two octahedra thick parallel to the *ac* plane. In the *b* direction, these layers are held together by hydrogen bonds. The occurrence in nature of an oxidized form, a triclinic symplesite-like phase, is considered to be highly probable.

Keywords: barićite, crystal structure, phosphate mineral, magnesium–iron phosphate.

SOMMAIRE

Nous avons affiné la structure cristalline de la barićite, l'analogue de la vivianite à dominance de Mg, $(Mg_{1.70}Fe^{2+}_{1.30-x}Fe^{3+}_{x})(PO_4)_2(OH)_x\bullet(8-x)H_2O$, a 10.085(2), b 13.390(3), c 4.6713(9) Å, β 104.96(3)°, V 609.4(1) Å^3, groupe spatial $C2/m$, $Z = 2$, $\rho_{calc} = 2.441$ g/cm^3 [diffractomètre à cristal unique automatisé, rayonnement Mo$K\alpha$, monochromatisation au graphite, détecteur à aire, T = 193 K, 5714 réflexions, $wR_2 = 0.106$ pour 1244 réflexions uniques, $R_1 = 0.043$ pour 965 réflexions observées pour lequelles $I \leq 2\sigma(I)$]. L'affinement de l'occupation des sites a montré que Fe et Mg sont partiellement désordonnés. Selon les résultats obtenus en diffraction X et en spectroscopie de Mössbauer, le site au centre de symétrie ($M1$) est essentielement occupé par le Fe, tandis que le Mg préfère la position $M2$, sur l'axe de rotation 2; les atomes Fe occupent deux-tiers des sites à coordinence octaédrique $M1$ et un-tiers des sites $M2$. Nous avons déterminé la position des quatre atomes independants d'hydrogène à partir des synthèses de Fourier par différence, et nous avons affiné ces positions en les considérant isotropes. La structure cristalline de la barićite contient deux types de fragments octaédriques: les octaèdres $M1O_2(H_2O)_4$ isolés et les dimères faits de deux octaèdres avec arête partagée. Dans la structure, ces modules octaédriques sont liés par les tétraèdres d'orthophosphate formant les couches d'une épaisseur de deux octaèdres, parallèles au plan *ac*. Le long de *b*, ces couches sont rattachées par liaisons hydrogène. Nous considérons très probable qu'une forme oxydée triclinique, semblable à la symplésite, existe dans la nature.

Mot-clés: barićite, structure cristalline, minéral phosphaté, phosphate de magnésium et de fer.

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INTRODUCTION

The rare mineral barićite was discovered by Sturman & Mandarino (1976) in low-temperature assemblages that fill fractures in a siderite-rich formation in the Big Fish River area, in the northeastern part of Yukon Territory, Canada, in association with quartz, fluorapatite, lazulite and magnesian vivianite. Two other occurrences of barićite have been described, by Rodgers (1987) and Liferovich *et al.* (1999).

Barićite is a member of the large group of natural and synthetic compounds that can be described with the common formula $M_3(TO_4)_2{\bullet}8H_2O$, where *M* represents Fe, Mg, Zn, Ni, Co, and Mn, and *T* represents P and As. The group is named after the most common mineral, vivianite, $Fe_3(PO_4)_2{\bullet}8H_2O$, the first member to have been investigated structurally (Mori & Ito 1950). The name "barićite" includes all members of the vivianite group in which the proportion of Mg is greater than any other cation (Sturman & Mandarino 1976). In Table 1, we have collated information on vivianite-group compounds that have been studied structurally. In addition, a manganese-dominant analogue of vivianite with Mn : (Mn + Fe) close to 0.5 has been mentioned in the literature (Nakano 1992), as well as the mineral arupite $Ni_3(PO_4)_2{\bullet}$ $8H_2O$ (Buchwald 1990), discovered in a meteorite. Parasymplesite $Fe_3(AsO_4)_2{\bullet}8H_2O$ (Sturman 1976) is an arsenate analogue of vivianite.

We undertook the present structural analysis of barićite $(Mg,Fe)_3(PO_4)_2{\bullet}8H_2O$, not investigated so far, with the aim to find the Mg and Fe distribution between the octahedral sites. A Mössbauer spectroscopic investigation of barićite was undertaken to shed light on the above-mentioned problem. We present here our results,

TABLE 1. CRYSTAL DATA FOR VIVIANITE-GROUP COMPOUNDS*

Mineral or Synthetic Compound	Unit-cell dimensions (Å)	β (°)	D_{calc} g/cm³	*M*1 – O, Å average, Å |δ|,** %	*M*2 – O, Å average, Å |δ|, %	*R*
Vivianite $Fe^{2+}{}_3(PO_4)_2{\bullet}8H_2O$ Fejdi *et al.* (1980)	*a* 10.086(3) *b* 13.441(4) *c* 4.703(2)	104.27(2)	2.69	2.028 – 2.215 2.152 3.9	2.095 – 2.158 2.132 1.1	0.041
Synthetic Mg phosphate $Mg_3(PO_4)_2{\bullet}8H_2O$ Takagi *et al.* (1986)	*a* 10.034(1) *b* 13.407(2) *c* 4.657(1)	105.09(1)	2.23	2.015 – 2.133 2.094 2.5	2.071 – 2.110 2.085 0.8	0.025
Barićite $(Mg_{1.70}Fe^{2+}{}_{1.19}Fe^{3+}{}_{0.11})(PO_4)_2$ $(OH)_{0.11}{\bullet}7.89H_2O$ our data***	*a* 10.085(2) *b* 13.390(3) *c* 4.6713(9)	104.96(3)	2.44	2.025 – 2.185 2.132 3.4	2.092 – 2.105 2.100 0.2	0.043
Synthetic Co phosphate $Co_3(PO_4)_2{\bullet}8H_2O$ Riou *et al.* (1989)	*a* 10.021(3) *b* 13.331(3) *c* 4.673(2)	104.91(1)	2.78	2.021 – 2.158 2.112 2.9	2.098 – 2.111 2.102 0.3	0.018
Erythrite $(Co_{2.01}Fe_{0.74}Ni_{0.25})(AsO_4)_2{\bullet}8H_2O$ Wildner *et al.* (1996)	*a* 10.251(3) *b* 13.447(4) *c* 4.764(1)	104.98(2)	3.14	2.029 – 2.160 2.116 2.8	2.099 – 2.118 2.106 0.4	0.027
Köttigite $(Zn_{2.44}Co_{0.42}Ni_{0.14})(AsO_4)_2{\bullet}8H_2O$ Hill (1979)	*a* 10.241(3) *b* 13.405(3) *c* 4.757(2)	105.21(1)	3.30	2.026 – 2.159 2.115 2.8	2.088 – 2.116 2.099 0.5	0.054
Synthetic (Mg,Ni) arsenate $(Mg_{2.48}Ni_{0.52})(AsO_4)_2{\bullet}8H_2O$ Rojo *et al.* 1996****	*a* 10.257(1) *b* 13.421(1) *c* 4.753(1)	105.10(1)	2.70	2.057 – 2.144 2.115 1.8	2.070 – 2.181 2.114 2.1	0.056
"Cabrerite" $(Ni_{2.2}Mg_{0.7}Fe_{0.1})(AsO_4)_2{\bullet}8H_2O$ Giuseppetti & Tadini (1982)	*a* 10.211(6) *b* 13.335(3) *c* 4.728(3)	104.97(6)	3.08	2.030 – 2.114 2.086 1.8	2.063 – 2.088 2.074 0.4	0.046
Annabergite $(Ni_{2.64}Mg_{0.36})(AsO_4)_2{\bullet}8H_2O$ Wildner *et al.* (1996)	*a* 10.179(2) *b* 13.309(3) *c* 4.725(1)	105.00(1)	3.15	2.031 – 2.114 2.086 1.8	2.054 – 2.092 2.073 0.6	0.015

* Space group *C* 2/*m*, *Z* = 2. ** $|\delta|$ is the polyhedron distortion, and is defined as $100/n \bullet (\Sigma|d_i - d_m| / d_m)$ %, where n is the number of cation–anion bonds in a polyhedron, d_i is the cation–anion distance, in Å, and d_m is the average cation–anion distance in a polyhedron. *** The low-temperature X-ray experiment. **** Powder-diffraction data, Rietveld refinement. "Cabrerite": magnesian annabergite.

together with that of an X-ray study carried out on a cotype specimen of barićite, described by Sturman & Mandarino (1976).

Background Information

The type-locality sample of barićite was kindly made available for this study by Dr. Göde Stümpel. The mineral occurs in pale blue plates up to 12 cm in maximum dimension and up to 5 cm thick. According to Sturman & Mandarino (1976), the type-locality barićite, as described here, is a ferroan variety, and the intensity of its blue color depends on the oxidation state of the iron. The ideal chemical formula they gave for the ferroan barićite is: $(Mg_{1.64}Fe^{2+}{}_{1.21}Fe^{3+}{}_{0.15})(PO_4)_2\ (OH)_{0.15}\bullet 7.85H_2O$.

Morphological, optical and chemical properties of barićite from the Big Fish River area were reported by Sturman & Mandarino (1976). The X-ray powder-diffraction pattern we obtained, with a DRON–2.0 diffractometer and Cu*K*α radiation (Ni filter), is very similar to the pattern of the holotype barićite (Sturman & Mandarino 1976).

There are two independent octahedral cationic positions in the vivianite structure-type, and these positions can be differently occupied by the cations. The *M*1 atoms occupy a crystallographic site with point symmetry 2/*m* and are coordinated by two oxygen atoms and four H_2O molecules. The *M*2 atoms are in the position at the two-fold axis (point symmetry 2), and their coordination polyhedron is formed by four oxygen atoms and two H_2O molecules. The possible site-preference of Mg or Fe atoms in the barićite structure (*M*1 or *M*2) is assessed in the present work. The second problem, in connection with barićite, is the possible occurrence of the oxidation of iron, which is well known for vivianite. The phenomenon of oxidation has been studied by different methods in vivianite (Dormann *et al.* 1982, Marincea *et al.* 1997). The oxidation of iron is associated with the transformation of H_2O molecules into hydroxyl groups. That process ends with a change in structure from monoclinic to triclinic, which characterizes the mineral metavivianite, the product of a partial oxidation of iron. According to Dormann *et al.* (1982), the same mechanism regulates the transformation of monoclinic parasymplesite $Fe_3(AsO_4)_2\bullet 8H_2O$ to triclinic symplesite, and could initiate the transformation of barićite to its triclinic equivalent. It would be interesting to know the limit of Fe^{3+} admission within the monoclinic structure of barićite, wich contains approximately equivalent quantities of Fe and Mg atoms.

Characterization of Barićite by Mössbauer Spectroscopy

Samples of barićite from the type locality were gently ground in an agate mortar with acetone to make a powder. No change in color was noted upon grinding. The powder was mixed with benzophenone to avoid preferred orientation, and loaded in a sample holder made of plexiglas. The sample weight was determined on the basis of the proportion of iron such that the dimensionless effective thickness of the sample was equal to 2 (corresponding to 5 mg Fe/cm^2), in order to minimize thickness effects.

Mössbauer spectra were recorded at room temperature (293 K) in transmission mode on a constant-acceleration Mössbauer spectrometer with a nominal 50 mCi ^{57}Co source in a 6 μm Rh matrix. The velocity scale was calibrated relative to 25 μm α-Fe foil using the positions certified for National Bureau of Standards standard reference material no. 1541; line widths of 0.28 mm/s for the outer lines of α–Fe were obtained at room temperature. The spectra were fitted using the commercially available fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany). The spectrum was collected over one day.

Data were fitted to four Lorentzian doublets, which were sufficient to account for all spectral absorption. The fitting model was chosen so as to (1) minimize the number of parameters, and (2) provide a physically realistic fit to the spectrum. Conventional constraints were applied to the high- and low-velocity components of each doublet (*i.e.,* equal area and equal width). No interspectrum constraints were applied.

Each spectrum (Fig. 1) contains two Fe^{2+} doublets that are sufficiently well resolved that model-independent hyperfine parameters were determined. The line widths of the two Fe^{2+} doublets are narrow, indicating that each doublet corresponds to a single site. Hyperfine parameters, given in Table 2, are similar to those reported for vivianite (Amthauer & Rossman 1984). Accordingly, the doublets were assigned to the *M*1 and *M*2 octahedral sites.

The Fe^{3+} absorption consists of at least two strongly overlapping doublets, and the line positions cannot be determined unambiguously. Two Fe^{3+} doublets were used, which is the minimum number of doublets required to fit the spectrum. The center shifts of the two doublets correspond to Fe^{3+} in octahedral coordination,

TABLE 2. HYPERFINE PARAMETERS DETERMINED FROM ROOM-TEMPERATURE (293 K) MÖSSBAUER DATA ON BARIĆITE

	CS mm/s	QS mm/s	FWHM mm/s	Area %
Fe^{2+} (*M*1)	1.18(1)	2.46(1)	0.27(1)	41(3)
Fe^{2+} (*M*2)	1.21(1)	3.26(1)	0.28(1)	50(3)
Fe^{3+} (*M*1)	0.31(2)	0.47(3)	0.31(3)	6(2)
Fe^{3+} (*M*2)	0.29(2)	1.11(3)	0.21(6)	3(2)

CS: center shift (relative to α-Fe); QS: quadruple splitting; FWHM: full-width at half maximum.

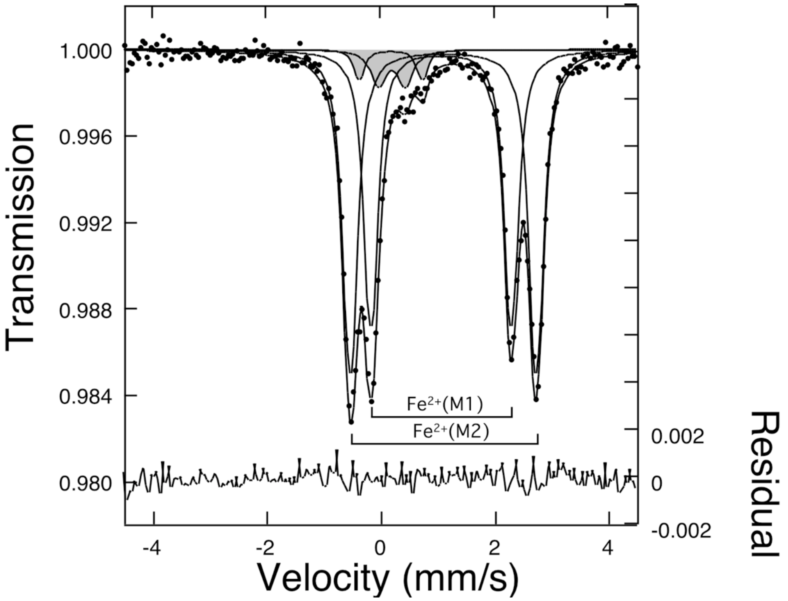

FIG. 1. Room-temperature Mössbauer spectrum of barićite. The ratio Fe^{3+}/Fe can be determined with a high degree of certainty, and Fe^{2+} doublets can be unambiguously assigned (unshaded); however, individual assignement of Fe^{3+} doublets are less certain (shaded grey).

and are tentatively assigned to the *M*1 and *M*2 sites of the structure. The relative areas in the spectrum give a first-order approximation of the site occupancies (Table 2). Although the Fe^{3+} doublets are not well resolved, the determination of Fe^{3+}/ Fe is still well determined, and uncertainties in Fe^{3+} doublets assignment contribute only a small uncertainty to the overall site-occupancies of iron.

The uncertainties given are based on errors derived from the fit to the given model, and uncertainties in the model itself. Not included are effects due to differences in recoil-free fraction and thickness effects, although both are estimated to be within the above uncertainties.

THE CRYSTAL STRUCTURE OF BARIĆITE

A light-blue single crystal of barićite from the type locality was selected for collection of X-ray data. The unit-cell parameters were determined and refined on an IPDS area-detector system (Stoe 1997) using Mo$K\alpha$ radiation (graphite monochromator). Because of the significant contents of H_2O in the mineral, the diffraction data for barićite were collected under low-temperature conditions (T = 193 K, nitrogen cooling), to get reliable results in the location and refinement of hydrogen atoms. The intensities were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction, based on a Ψ scan to measure equivalents, was applied using equivalent reflections. In Table 3, we report the crystallographic characteristics and the experimental conditions of data collection and refinement.

All calculations were performed with the SHELXL–97 program (Sheldrick 1997). Atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography (Hahn 1995). Starting with the atom coordinates of vivianite (Fejdi *et al.* 1980), we refined the structure of barićite using the F^2 data to residuals $wR_2 = 0.106$ (for all 1244 reflections) and $R = 0.043$ [for 965 reflections > $2\sigma(I)$], with anisotropic displacement parameters for all non-H atoms.

Refinement of site occupancies showed that Fe and Mg atoms are partially ordered in the structure. According to the X-ray data, Fe mainly occupies the site at the center of symmetry (*M*1), whereas Mg prefers the position at the two-fold axis (*M*2). During the refinement, the atom-displacement parameters of Mg and Fe were constrained to be equal. We determined the following site-occupancies for the *M*1 [0.63(1) Fe + 0.37(1) Mg] and *M*2 sites [0.665(7) Mg + 0.335(7) Fe]. These inferred occupancies corresponds to the formula: $(Mg_{1.70}Fe_{1.30})(PO_4)_2{\bullet}8H_2O$. These site occupancies are equal within experimental error to those determined by Mössbauer spectroscopy: *M*1 [0.61(5) Fe + 0.39(5) Mg] and *M*2 [0.66(3) Mg + 0.34(3) Fe]. On the basis of X-ray and spectroscopic results, we can write the follow-

TABLE 3. CRYSTAL DATA AND DETAILS OF THE COLLECTION AND REFINEMENT OF X-RAY DATA FOR BARIĆITE

Crystal data	
Formula	$(Mg_{1.70} Fe_{1.30})(PO_4)_2 \cdot 8H_2O$
Absorption μ [mm^{-1}]	2.024
Space group	*C2/m*, *Z* = 2
Unit-cell volume *V* (Å^3)	609.4(2)
Density (g cm^{-3}) d_{calc}	2.441
Data collection	
Diffractometer	IPDS – II area-detector system (Stoe)
Radiation	MoKα, graphite monochromator
Temperature (K)	193
Scanning mode	Φ = 0–200°, δΦ = 1°, 3 min/rec
Measuring range	max θ = 33.8°
Reflections (total)	5714
R_{int}	0.0597
R_σ	0.0397
Refinement	
Reflections unique/observed [I>2σ(I)]	1244/965
Parameters	74
Absorption correction	semiempirical with equivalents (ψ scan)
T_{max}, T_{min}	0.8554, 0.6764
Extinction coefficient	0.019(3)
Residuals R (observed reflections)	0.0430
R, wR$_2$ (all reflections)	0.0612, 0.1058
Goodness of fit S	1.036
δρ (max)	0.694
δρ (min)	–0.796

ing structural formula, at least for the sample of barićite we investigated: $(Fe^{2+}_{0.55}Mg_{0.37}Fe^{3+}_{0.08})_{M1}(Mg_{1.33}Fe^{2+}_{0.64}Fe^{3+}_{0.03})_{M2}[PO_4]_2(OH)_{0.11} \cdot 7.89H_2O$ ($Z = 2$, $D_{calc} = 2.441$ g/cm^3). Our formula is in a good agreement with the formula given by Sturman & Mandarino (1976) for the type-locality barićite ($D_m = 2.42$ g/cm^3).

The positions of four independent H atoms were obtained from difference-Fourier syntheses and were refined under isotropic approximation. The final atom coordinates and interatomic distances are given in Table 4 and 5. Table 6 presents the geometrical characteristics of the hydrogen bonds. The results of the bond-valence analysis (Pyatenko 1972, Brown 1976) are given in Table 7. A table of structure factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

INTERATOMIC DISTANCES IN BARIĆITE

Four of the vertices of the *M*1 octahedron are occupied by O atoms of H_2O molecules (henceforth O_W) and two vertices, by *trans*-positioned O atoms of phosphate groups (henceforth O_P). The interatomic distances *M*1 – O_W, 2.185(2) Å are, as expected, larger than the distances *M*1 – O_P, 2.025(2) Å. Four O_P and two O_W in a *cis* configuration form the coordination polyhedron *M*2. In that octahedron, the interatomic distances *M*2–O_W, 2.092(2) Å, are actually shorter than the *M*2 – O_P distances [2.104(2), 2.105(2) Å], which are identical within one standard deviation. The average cation – anion dis-

TABLE 4A. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR BARIĆITE, CONSIDERED AS A BINARY SOLID-SOLUTION

Atom	Wyckoff position	*x*	*y*	*z*	*U*(eq)
Fe(1)^a	2c	0.0	0.0	0.5	0.0111(3)
Mg(1)^b	2c	0.0	0.0	0.5	0.0111(3)
Fe(2)^c	4h	0.5	0.11050(5)	0.5	0.0109(3)
Mg(2)^d	4h	0.5	0.11050(5)	0.5	0.0109(3)
P	4i	0.68507(8)	0.0	0.11955(17)	0.0107(2)
O(1)	4i	-0.3946(2)	0.0	-0.2084(5)	0.0133(4)
O(2)	4i	-0.1582(2)	0.0	0.1307(5)	0.0137(4)
O(3)	8j	-0.65471(16)	0.09621(12)	-0.2743(4)	0.0135(3)
O(4)	8j	0.10049(18)	0.11636(13)	0.3037(4)	0.0158(3)
O(5)	8j	-0.60123(19)	0.22338(14)	-0.7828(4)	0.0184(4)

occupancy: ^{a} 0.63(1), ^{b} 0.37(1), ^{c} 0.335(7), ^{d} 0.665(7).
U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

TABLE 4B. ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR BARIĆITE

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0081(4)	0.0138(4)	0.0103(4)	0.0	0.0005(3)	0.0
Fe(2)	0.0094(3)	0.0122(4)	0.0105(4)	0.0	0.0018(2)	0.0
Mg(1)	0.0081(4)	0.0138(4)	0.0103(4)	0.0	0.0005(3)	0.0
Mg(2)	0.0094(3)	0.0122(4)	0.0105(4)	0.0	0.0018(2)	0.0
P	0.0084(3)	0.0130(4)	0.0101(3)	0.0	0.0014(2)	0.0
O(1)	0.0107(9)	0.0158(10)	0.0125(9)	0.0	0.0012(7)	0.0
O(2)	0.0097(9)	0.0177(10)	0.0131(10)	0.0	0.0020(8)	0.0
O(3)	0.0126(7)	0.0141(7)	0.0132(7)	0.0012(5)	0.0025(5)	0.0008(5)
O(4)	0.0127(7)	0.0188(8)	0.0152(7)	-0.0003(5)	0.0021(6)	0.0001(6)
O(5)	0.0211(8)	0.0171(8)	0.0170(8)	0.0003(6)	0.0049(6)	0.0008(6)

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [\, h^2 a^{*2} U_{11} + \ldots\ldots + 2\, h\, k\, a^*\, b^*\, U_{12}]$.

TABLE 4C. HYDROGEN COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR BARIĆITE

	x	*y*	*z*	U_{iso}
H(1)	0.134(4)	0.094(3)	0.152(9)	0.022(9)
H(2)	-0.554(4)	0.280(3)	-0.794(10)	0.030(10)
H(3)	0.180(5)	0.122(3)	0.439(11)	0.031(10)
H(4)	-0.623(5)	0.203(3)	-0.958(11)	0.034(11)

TABLE 5. BOND LENGTHS (Å) IN BARIĆITE

*M*1 octahedron		*M*2 octahedron		P tetrahedron	
*M*1 – O2	2.025(2) ×2	*M*2 – O5	2.092(2) ×2	P – O1	1.535(3)
– O4	2.185(2) ×4	– O3	2.104(2) ×2	– O3	1.546(2) ×2
		– O1	2.105(2) ×2	– O2	1.568(2)
average	2.132	average	2.100	average	1.549

TABLE 6. H-BONDING IN BARIĆITE

D –H ··· *A*	*D*–H, Å	H ··· *A*, Å	*D* ··· *A*, Å	∠*D*–H ··· *A*, °
O4 – H1 ··· O2	0.91(4)	1.89(4)	2.737(3)	155(4)
O4 – H3 ··· O3	0.89(5)	1.88(5)	2.746(3)	164(4)
O5 – H2 ··· O4	0.91(4)	2.05(4)	2.912(3)	159(4)
O5 – H4 ··· O3	0.83(5)	2.03(5)	2.797(3)	153(4)

D: donor, *A*: acceptor.

TABLE 7. BOND-VALENCE ANALYSIS FOR BARIĆITE

Cation Anion	*M*1	*M*2	P	H1	H2	H3	H4	Σ	δ
O1		0.331 0.331	1.344					2.006	0.006
O2	0.429		1.129	0.20 0.20				1.958	0.042
O3		0.331	1.263			0.20	0.17	1.964	0.036
O4	0.286			0.80	0.13	0.80		2.016	0.016
O5		0.338			0.87		0.83	2.038	0.038
Σ	2.002	2.000	4.999	1.000	1.000	1.000	1.000	Σδ =	0.138

D = (0.138 : 10) × 100% = 1.4% (Pyatenko 1972)

tances in the *M*1octahedra (2.132 Å) are somewhat larger than those in the *M*2 octahedra (2.100 Å), in agreement with the higher proportion of the Fe^{2+} ion (radius 0.78 Å) at *M*1 as compared with Mg^{2+} (0.72 Å). We assume, in this discussion, that the influence of Fe^{3+} is negligible. The *M*2 site is much less distorted than *M*1 (Table 5). The same situation can be found in the crystal structures of the other members of the vivianite family. Large differences among the individual *M*1–O bonds (Table 1) show the significant distortion of *M*1 polyhedra in all structures (exept for synthetic $(Mg,Ni)_3(AsO_4)_2 \cdot 8H_2O$ refined using powder-diffraction data), whereas *M*2 octahedra are rather regular in all cases, except in the synthetic Mg,Ni arsenate. We agree with the conclusion made by Giuseppetti & Tadini (1982) that the varying distortions of *M*1 and *M*2 octahedra in the vivianite structure-type depend mainly on the articulation of the polyhedra surrounding by the other structural units rather than on the nature of the central cation. The results of our investigation of the barićite structure confirm also the conclusion of Giuseppetti & Tadini (1982), that transition metals prefer the more distorted *M*1 octahedra. Thus, the distribution of Fe and Mg atoms in barićite tends to follow the above-mentioned rule: Fe atoms (both Fe^{2+} and Fe^{3+}) occupy two-thirds of the *M*1 and one-third of the *M*2 octahedra.

The P–O interatomic distances in the orthophosphate tetrahedron are in the range 1.535(3)–1.568(3) Å and correlate well with similar bond-lengths in the structures of vivianite and of synthetic Mg and Co analogues (Table 1).

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of barićite (Fig. 2) consists of two types of structural units: isolated $M1O_2(H_2O)_4$ octahedra and clusters of two edge-sharing polyhedra $M2O_6(H_2O)_4$. These octahedral units are connected in the structure by orthophosphate tetrahedra to form layers two octahedra thick parallel to the *ac* plane. This structural feature, layers of octahedra and tetrahedra, explains the flattened habit and the perfect cleavage of the crystals, mentioned by Sturman & Mandarino (1976). The unit cell of barićite contains two layers of this kind. In the *b* direction, these layers are held together by hydrogen bonds (Table 5). All the oxygen atoms, except O1, are involved in the system of hydrogen bonds of the barićite structure. The oxygen atom of H_2O molecule O4 is not only the donor of two hydrogen bonds, but plays also the function of a hydrogen-bond acceptor. Both O2 and O3 atoms act as acceptors of two hydrogen bonds.

The X-ray-diffraction study cannot prove quantitatively whether any Fe^{3+} is present in the structure. Interatomic distances and bond-valence analysis agree well with the assumption of Fe^{2+} in both octahedra. At the same time, a small amount of oxidized iron in *M*1 position was found by Mössbauer spectroscopy. It has been shown (Dormann *et al.* 1982) for the köttigite–parasymplesite solid solution, $Zn_xFe_{3-x}(AsO_4)_2 \cdot 8H_2O$, that a monoclinic → triclinic structural transformation takes place if half of the atoms in *M*1 positions are in the oxidized form. For that chemical composition the oxidized variety can exist with at least 50% iron occupancy of the *M*1 position. Expanding that conclusion to isotypic barićite, with 2/3 Fe atoms in *M*1 position and a small amount of the Fe in the oxidized form, as has been shown here, we predict a high probability of occurrence of a triclinic variety in nature. For the hypothetical fully oxidized phase with the Mg:Fe ratio we found, and in agreement with the data of Dormann *et al.* (1982) for metavivianite, we would predict the following formula: $Fe^{3+}_{1.30}Mg_{1.70}(PO_4)_2(OH)_{1.30} \cdot 6.7H_2O$.

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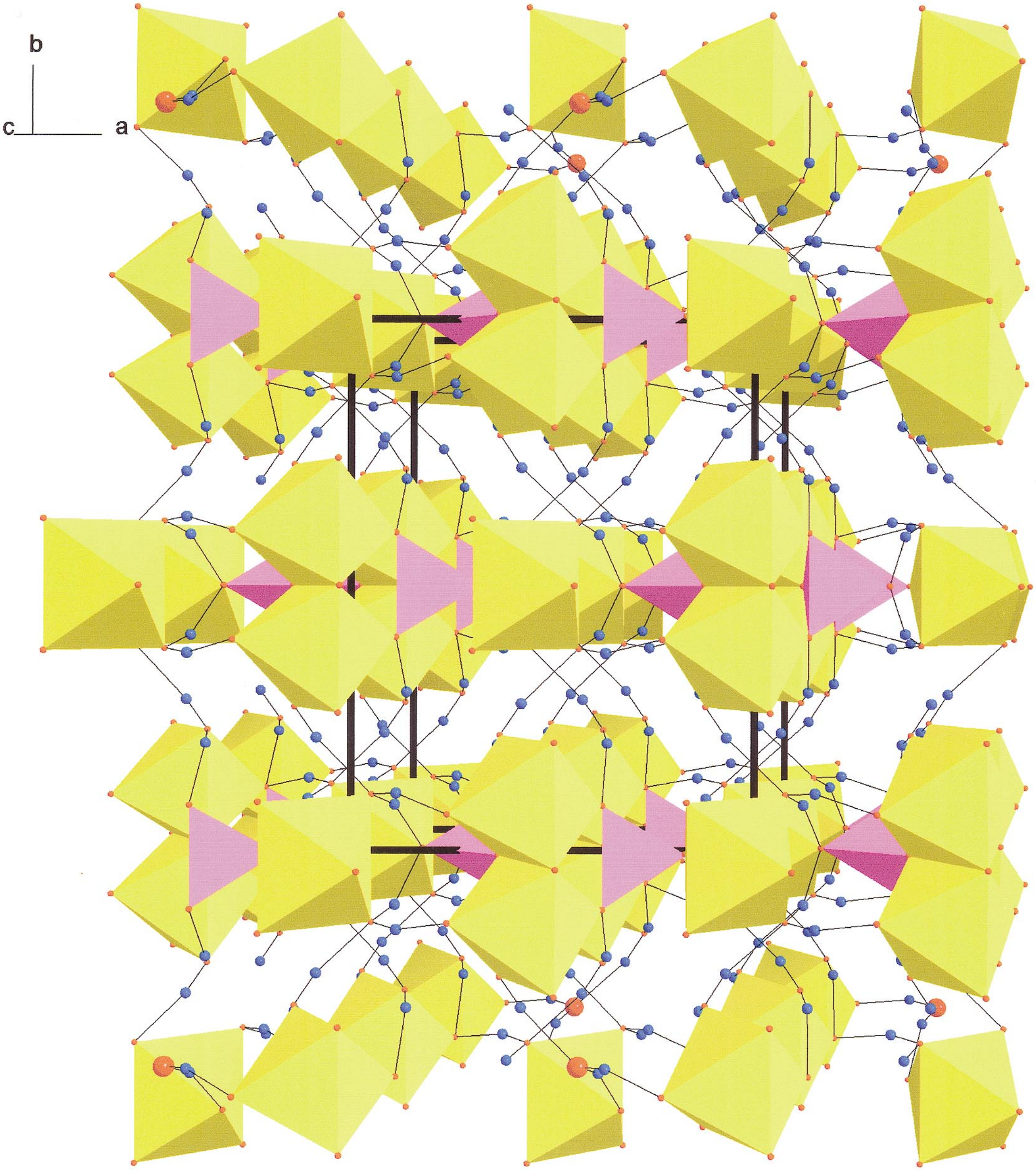

FIG. 2. Crystal structure of barićite. Perspective view along a direction close to [001]. The green-yellow octahedra contain Mg and Fe. The pink tetrahedra contain the phosphorus. Oxygen and hydrogen atoms are illustrated with orange and blue spheres, respectively.

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REFERENCES

AMTHAUER, G. & ROSSMAN, G.R. (1984): Mixed valence of iron in minerals with cation clusters. *Phys. Chem. Minerals* **11**, 37-51.

BROWN, I.D. (1976): On the geometry of O–H...O hydrogen bonds. *Acta Crystallogr.* **A32**, 24-31.

BUCHWALD, V.F. (1990): A new mineral, arupite, $Ni_3(PO_4)_2$•$8H_2O$, the nickel analogue of vivianite. *Neues Jahrb. Mineral., Monatsh.,* 76-80.

DORMANN, J.-L., GASPÉRIN, M. & POULLEN, J.-F. (1982): Étude structurale de la séquence d'oxydation de la vivianite $Fe_3(PO_4)_2$•$8H_2O$. *Bull. Minéral.* **105**, 147-160.

FEJDI, P., POULLEN, J.-F. & GASPÉRIN, M. (1980): Affinement de la structure de la vivianite $Fe_3(PO_4)_2$•$8H_2O$. *Bull. Minéral.* **103**, 135-138.

GIUSEPPETTI, G.& TADINI, C. (1982): The crystal structure of cabrerite, $(Ni,Mg)_3(AsO_4)_2$•$8H_2O$, a variety of annabergite. *Bull. Minéral.* **105**, 333-337.

HAHN, T., ed. (1995): *International Tables for Crystallography.* Vol. **A** (4th ed.). Kluwer Acad. Publ., Dordrecht, The Netherlands.

HILL, R.J. (1979): The crystal structure of köttigite. *Am. Mineral.* **64**, 376-382.

LIFEROVICH, R.P., PAKHOMOVSKY, YA. A., BOGDANOVA, A.N. & BAKHCHITSARAITSEV, A.YU. (1999): Barićite from the Kovdor massif – first occurrence in Russia. *European Geological Congress EUG-10* (*Strasbourg*), 496.

MARINCEA, Ş., CONSTANTINESCU, E. & LADRIÈRE, J. (1997): Relatively unoxidized vivianite in limnic coal from Capeni, Baraolt Basin, Romania. *Can. Mineral.* **35**, 713-722.

MORI, H. & ITO, T. (1950): The structure of vivianite and symplesite. *Acta Crystallogr.* **3**, 1-6.

NAKANO, S. (1992): Manganoan vivianite in the bottom sediments of the lake Biwa, Japan. *Mineral. J.* **16**, 96-107.

PYATENKO, YU.A. (1972): Unified approach to analysis of local balance of valences in inorganic structures. *Sov. Phys. Crystallogr.* **17**, 677-682.

RIOU, A., CUDENNEC, Y. & GERAULT, Y. (1989): Cobalt (II) orthophosphate octahydrate. *Acta Crystallogr.* **C45**, 1412-1413.

RODGERS, K.A. (1987): Barićite, a further occurrence. *Neues Jahrb. Mineral., Monatsh.*, 183-192.

ROJO, J.M., MESA, J.L., PIZARRO, J.L., LEZAMA, L., ARRIORTUA, M.I. & ROJO, T. (1996): Spectroscopic and magnetic study of the $(Mg, M)_3(AsO_4)_2$•$8H_2O$ (M = Ni($^{2+}$), Co ($^{2+}$)) arsenates. *Mat. Res. Bull.* **31**, 925-934.

SHELDRICK, G.M. (1997): *SHELXL-97: Program for the Refinement of Crystal Structures*. University of Göttingen, Göttingen, Germany.

STOE & CO. (1997): *IPDS. Image Plate Detector System.* Version 2.86. GmbH, Darmstadt, Germany.

STURMAN, B.D. (1976): New data for köttigite and parasymplesite. *Can. Mineral.* **14**, 437-441.

________ & MANDARINO, J.A. (1976): Barićite, the magnesian analogue of vivianite from Yukon Territory, Canada. *Can. Mineral.* **14**, 403-406.

TAKAGI, S., MATHEW, M. & BROWN, W.E. (1986): Crystal structures of bobierrite and synthetic $Mg_3(PO_4)_2$•$8H_2O$. *Am. Mineral.* **71**, 1229-1233.

WILDNER, M., GIESTER, G., LENGAUER, C.L. & MCCAMMON, C.A. (1996): Structure and crystal chemistry of vivianite-type compounds: crystal structures of erythrite and annabergite with a Mössbauer study of erythrite. *Eur. J. Mineral.* **8**, 187-192.

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