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Footemineite, the Mn-analog of atencioite, from the Foote mine, Kings Mountain, Cleveland County, North Carolina, U.S.A., and its relationship with other roscherite-group minerals

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ABSTRACT

Footemineite, ideally $Ca_2Mn^{2+}\square Mn^{2+}_2Mn^{2+}_2Be_4(PO_4)_6(OH)_4{\cdot}6H_2O$, triclinic, is a new member of the roscherite group. It occurs on thin fractures crossing quartz-microcline-spodumene pegmatite at the Foote mine, Kings Mountain, Cleveland County, North Carolina, U.S.A. Associated minerals are albite, analcime, eosphorite, siderite/rhodochrosite, fairfieldite, fluorapatite, quartz, milarite, and pyrite. Footemineite forms prismatic to bladed generally rough to barrel-shaped crystals up to about 1.5 mm long and 1 mm in diameter. Its color is yellow, the streak is white, and the luster is vitreous to slightly pearly. Footemineite is transparent and non-fluorescent. Twinning is simple, by reflection, with twin boundaries across the length of the crystals. Cleavage is good on $\{0\bar{1}1\}$ and {100}. Density (calc.) is 2.873 g/cm^3. Footemineite is biaxial (–), $n_\alpha = 1.620(2)$, $n_\beta = 1.627(2)$, $n_\gamma = 1.634(2)$ (white light). $2V_{obs} = 80°$, $2V_{calc} = 89.6°$. Orientation: X ^ *b* ~ 12°, Y ^ *c* ~ 15°, Z ^ *a* ~ 15°. Elongation direction is *c*, dispersion: r > v or r < v, weak. Pleochroism: β (brownish yellow) > α = γ (yellow). Mössbauer and IR spectra are given. The chemical composition is (EDS mode electron microprobe, Li and Be by ICP-OES, Fe^{3+}:Fe^{2+} by Mössbauer, H_2O by TG data, wt%): Li_2O 0.23, BeO 9.54, CaO 9.43, SrO 0.23, BaO 0.24, MgO 0.18, MnO 26.16, FeO 2.77, Fe_2O_3 0.62, Al_2O_3 0.14, P_2O_5 36.58, SiO_2 0.42, H_2O 13.1, total 99.64. The empirical formula is $(Ca_{1.89}Sr_{0.03}Ba_{0.02})_{\Sigma 1.94}(Mn^{2+}_{0.90}\square_{0.10})_{\Sigma 1.00}(\square_{0.78}Li_{0.17}Mg_{0.05})_{\Sigma 1.00}(Mn^{2+}_{3.25}Fe^{2+}_{0.43}Fe^{3+}_{0.09}Al_{0.03})_{\Sigma 3.80}Be_{4.30}(P_{5.81}Si_{0.08}O_{24})[(OH)_{3.64}(H_2O)_{0.36}]_{\Sigma 4.00}{\cdot}6.00H_2O$. The strongest reflection peaks of the powder diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are 9.575 (53) (010), 5.998 (100) $(0\bar{1}1)$, 4.848 (26) (021), 3.192 (44) (210), 3.003 (14) $(0\bar{2}2)$, 2.803 (38) $(\bar{1}03)$, 2.650 (29) $(\bar{2}02)$, 2.424 (14) (231). Single-crystal unit-cell parameters are $a = 6.788(2)$, $b = 9.972(3)$, $c = 10.014(2)$ Å, $\alpha = 73.84(2)$, $\beta = 85.34(2)$, $\gamma = 87.44(2)°$; $V = 648.74$ Å^3, $Z = 1$. The space group is $P\bar{1}$. Crystal structure was refined to $R = 0.0347$ with 1273 independent reflections ($F > 2\sigma$). Footemineite is dimorphous with roscherite, and isostructural with atencioite. It is identical with the mineral from Foote mine described as "triclinic roscherite." The name is for the Foote mine, type locality for this and several other minerals.

Keywords: Footemineite, new mineral, roscherite-group, Mn-phosphate, crystal structure, atencioite, Foote mine, North Carolina

INTRODUCTION

As it was demonstrated by our recent investigations (Chukanov et al. 2002, 2006, 2007; Rastsvetaeva et al. 2002, 2004a, 2004b, 2005; Barinova et al. 2004; Atencio et al. 2005; Chukanov and Möckel 2005), roscherite-group minerals are notable for a wide diversity of their chemical composition and cation ordering. Most of them are monoclinic, with predominance of Mn, Mg, Fe^{2+}, Fe^{3+}, or Zn in the group of octahedral cations. Up to now only one triclinic member of this group, atencioite, has been approved by the IMA-CNMMN. In this mineral lowering of symmetry is connected with the ordering of Fe^{2+}, Fe^{3+}, Mg, and vacancies in sites with octahedral coordination. Footemineite, $Ca_2Mn^{2+}\square Mn^{2+}_2Mn^{2+}_2Be_4(PO_4)_6(OH)_4{\cdot}6H_2O$, is a new, Mn-rich triclinic species of the roscherite group. The name is for the Foote mine, type locality for this mineral and also brannockite, eakerite, earlshannonite, kingsmountite, lithiomarsturite, mangangordonite, metaswitzerite, swinefordite, switzerite, and tetrawickmanite. The name "footeite" was used for a mineral (later discredited as connellite) in honor of the mineral dealer A.E. Foote who started the Foote Mineral Company. The new mineral has been approved by the CNMMN-IMA (vote 2006-029).

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Holotype material is deposited under the number DR601 in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080, São Paulo, SP, Brazil, and in the Museu de Ciências Naturais Jobas "José Bonifácio de Andrada e Silva," Santos, SP, Brazil.

The mineral described in this paper is identical with that of Fanfani et al. (1977), described as "triclinic roscherite;" both materials are from the same locality, the Foote mine. In databases the "triclinic roscherite" by Fanfani et al. (1977) is also referred to under different names as "roscherite-1A" or "roscherite (C-1)." Some databases even give erroneously only triclinic symmetry for roscherite. The naming (and description) of footemineite as a mineral dimorphous with roscherite (=monoclinic) should put an end to this confusion.

OCCURRENCE

Footemineite occurs in a quartz-microcline-spodumene pegmatite at the Foote Lithium Co. Mine (Foote Mine), Kings Mountain, Cleveland Co., North Carolina, U.S.A. The mineral was collected from the dumps. It forms crystals in thin fractures crossing a small block of pegmatite. Associated minerals are (in order of decreasing abundance): albite, analcime, eosphorite, siderite/rhodochrosite, fairfieldite, fluorapatite, quartz, milarite, and pyrite. This mineral was also collected in a different paragenesis many years ago when the quarry was active. Several other phosphates have been mentioned from this quarry (www.mindat.org). Footemineite is a late fracture-filling mineral.

APPEARANCE AND PHYSICAL PROPERTIES

Footemineite forms prismatic to bladed, generally rough to barrel-shaped crystals up to about 1.5 mm long and 1 mm in diameter. The faces making up the sides of the "barrels" are curved (Fig. 1). The crystals are similar to those of zanazziite (Leavens et al. 1990). Its color is yellow, the streak is white, and the luster is vitreous to slightly pearly. Footemineite is transparent and non-fluorescent. Mohs hardness is probably about 4½ to 5 by analogy with other roscherite-group minerals. Observed forms are pinacoids. Twinning is simple, by reflection, with twin boundaries across the length of the crystals. Cleavage is good on $\{0\bar{1}1\}$ and $\{100\}$ (which correspond, respectively, to $\{010\}$ and $\{001\}$ in the monoclinic roscherite-group minerals). The mineral is brittle. Fracture was not determined. Density was not measured due to the small amount of material available for study. Density (calc.) is 2.873 g/cm^3.

OPTICAL PROPERTIES AND SPECTROSCOPY

Footemineite is biaxial (–), $n_\alpha = 1.620(2)$, $n_\beta = 1.627(2)$, $n_\gamma = 1.634(2)$ (white light). $2V_{obs} = 80°$, $2V_{calc} = 89.6°$. Orientation: $X \wedge b \sim 12°$, $Y \wedge c \sim 15°$, $Z \wedge a \sim 15°$. Elongation direction is *c*, dispersion: r > v or r < v, weak. Pleochroism: β (brownish yellow) > $\alpha = \gamma$ (yellow).

Wavenumbers of the bands in IR spectrum are (Fig. 2; cm^{-1}; s = strong band, sh = shoulder): 3580sh, 3500sh, 3480, 3350, 3200sh (stretching vibrations of OH groups and H_2O molecules), 1665 (bending vibrations of H_2O molecules), 1100sh, 1075s, 1028s, 1015sh, 970sh, 950sh (stretching vibrations of PO_4^{3-} anions), 810, 762, 720, 695sh (stretching vibrations of BeO_4-tetrahedra and bending vibrations of M-OH fragments where M is octahedral cation), 611, 555 (bending vibrations of PO_4^{3-} anions), 522, 490, 475, 460, 445 (stretching vibrations of MO_6-octahedra). In comparison to monoclinic roscherite-group minerals, footemineite shows splitting of some P-O-stretching (1028 + 1015 cm^{-1}) and Be-O-stretching (the range 695–810 cm^{-1}) bands and presence of multiple bands in the range of stretching vibrations of octahedra, i.e., 445–522 cm^{-1}. Based on our data, triclinic roscherite-group minerals footemineite and atencioite show characteristic splitting of several bands, whereas in spectra of all monoclinic minerals of this group (roscherite, greifensteinite, zanazziite, 2005-061, guimarãesite) this splitting is absent.

Mössbauer spectrum of footemineite (Fig. 3) has been obtained with the modified WISSEL spectrometer, simultaneously in 512 channels during 240 h. The only strong doublet (with maxima of components at –0.1 and 2.1 mm/s) present in Mössbauer spectrum corresponds to Fe^{2+} (very close to Fe^{2+} in greifensteinite where all iron is Fe^{2+}). High dispersion of points on Figure 3 is due to low content of Fe in footemineite and lack of material available. For this reason some details of fine structure of the Mössbauer spectrum are unclear. Good approximation of the spectral curve is possible only under the condition $0 \leq Fe^{3+}:(Fe^{3+} + Fe^{2+}) \leq 0.2$ [the approximation on Fig. 3 corresponds to $Fe^{3+}:(Fe^{3+} + Fe^{2+}) = 0.2$]. Although the quality of Mössbauer spectrum is poor (due to low content of Fe in the mineral and deficit of substance available), it fully excludes a possibility that Fe^{3+} prevails over Fe^{2+}. The intensity of the component at 2 mm/s is comparable with that at 0 mm/s. It means that $Fe^{2+} >> Fe^{3+}$ and that $Fe^{3+} << 0.5$ apfu. For this reason Fe^{3+} cannot dominate in any site. The existence of a fine structure of Mössbauer spectrum (i.e., the state of Fe^{2+} cannot be described by only one doublet) indicates that Fe^{2+} is distributed (as admixture to Mn) among several different sites.

CHEMICAL DATA

Three point analyses (Table 1) have been carried out by means of an electron microprobe (EDS mode, 15.7 kV, 0.5 nA, 8 μm beam diameter). Lithium and Be were determined by ICP-OES using the VISTA-PRO device (analyst A.A. Agakha-

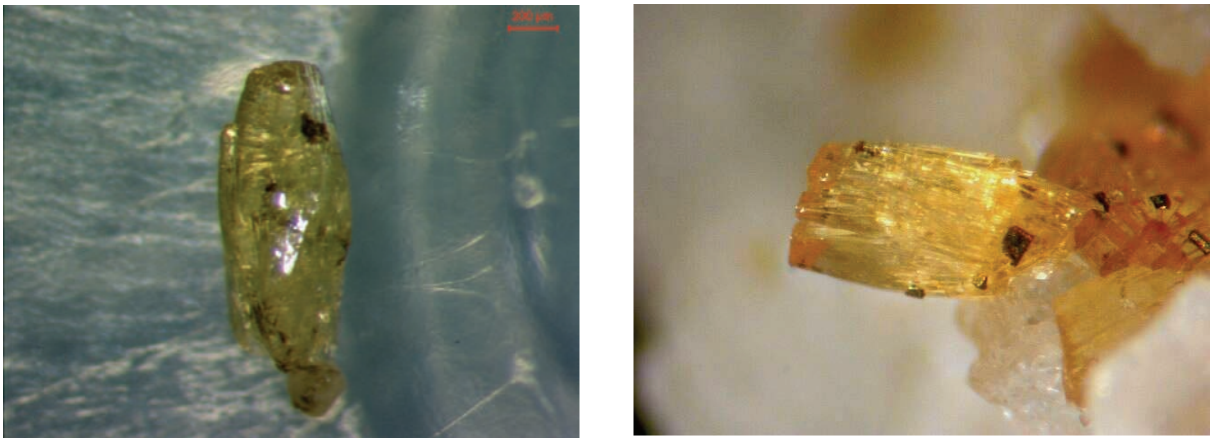

FIGURE 1. Footemineite crystals from Foote Lithium Co. Mine (Foote Mine), Kings Mountain District, Cleveland Co., North Carolina, U.S.A. The crystal in the second photo (J.B. Smith specimen no. 4471 and photo) measures 0.8 mm. Note the association with pyrite.

nov). H_2O was analyzed by weight loss in vacuum at 1000 °C. Mössbauer spectrum shows that most part of Fe is analogous to Fe^{2+} in M sites of other roscherite-group minerals; possible content of Fe^{3+} is ≤20% of total Fe. Close association with pyrite (an indication of reduction conditions of mineral formation) is in agreement with predominantly bivalent state of Fe. The supposition that Fe is trivalent in this mineral (Fanfani et al. 1977) was not confirmed. The empirical formula, based on 34 anions, is $(Ca_{1.89}Sr_{0.03}Ba_{0.02})_{\Sigma 1.94}(Mn^{2+}_{0.90}\square_{0.10})_{\Sigma 1.00}(\square_{0.78}Li_{0.17}Mg_{0.05})_{\Sigma 1.00}$ $(Mn^{2+}_{3.25}Fe^{2+}_{0.43}Fe^{3+}_{0.09}Al_{0.03})_{\Sigma 3.80}Be_{4.30}(P_{5.81}Si_{0.08}O_{24})[(OH)_{3.64}(H_2O)_{0.36}]_{\Sigma 4.00}\cdot 6.00H_2O$. The simplified formula is $Ca_2Mn^{2+}\square Mn^{2+}_2Mn^{2+}_2Be_4(PO_4)_6(OH)_4\cdot 6H_2O$, which requires: BeO 8.80, CaO 9.87, MnO 31.19, P_2O_5 37.46, H_2O 12.68, total 100.00 wt%.

CRYSTALLOGRAPHY

X-ray powder-diffraction data (obtained by means of a Philips MPD 1880 diffractometer using Cu*K*α radiation and 40 kV and 40 mA) are represented in Table 2. Interplanar distances and intensities agree very well with those calculated by Fanfani et al. (1977) (ICDD cards 30–173 and 83–1529). Footemineite is triclinic, space group: $P\bar{1}$. Unit-cell parameters refined from powder diffraction data are a = 6.742(3), b = 9.883(8), c = 9.981(6) Å, α = 74.12(6), β = 86.10(4), γ = 87.36(5)°; V = 637.9(7) Å^3. The *a:b:c* ratio is 0.6822:1:1.0099.

A single crystal of dimensions 0.10 × 0.15 × 0.25 mm was selected for intensity measurements on a Xcalibur single-crystal diffractometer with CCD detector using graphite-monochromatized Mo*K*α radiation. Single-crystal unit-cell parameters are a = 6.788(2), b = 9.972(3), c = 10.014(2) Å, α = 73.84(2), β = 85.34(2), γ = 87.44(2)°; V = 648.74 Å^3. The *a:b:c* ratio is 0.6807:1:1.0042. Compatibility 1 – (K_P/K_C) is –0.008 (superior) with $D_{calc.}$ Transformation from *P* cell to *C* pseudo-cell is carried out by the matrix $011/01\bar{1}/\bar{1}00$. Corresponding parameters of the pseudo-monoclinic unit cell are a = 15.978, b = 12.006, c = 6.788 Å, α = 88.24, β = 94.52, γ = 90.25°. Reflections $-10 \leq h \leq 10$, $-13 \leq k \leq 17$, $-15 \leq l \leq 18$ were used for structure refinement. Total number of reflections ($F > 2\sigma$) is 3094. Crystal structure was refined to $R = 0.0347$ with 1273 independent reflections. The atomic coordinates of atencioite were used as starting values in the refinement. From a difference Fourier map D2 position was located and refined as Li + Mg with very low occupancy. The absorption correction was made by DIFABS program (Walker and Stuart 1983). Table 3 presents the results of site refinement obtained using AREN program (Andrianov 1987), and Table 4 presents the bond distances. The shorter distance within the D2 octahedron (1.527) is due to the very low population of the site and to partial replacement of a water molecule by an OH group. Bond-valence balance for footemineite is presented in Table 5. Deficit of sums (last column in Table 5) for O3, O5, O10, and O11 is compensated by hydrogen atoms because they are acceptors of hydrogen bonds. These hydrogen bonds were analyzed previously for isostructural atencioite (Rastsvetaeva et al. 2004b) where (unlike footemineite) hydrogen atoms were localized. The total value of 0.52 v.u. (valence units) for D2 does not have any physical sense because valence balance cannot be calculated (and never is calculated) for sites with mixed (statistical) population. Each local situation should be considered separately. Calculated and observed structure factors are provided in Table 6[1].

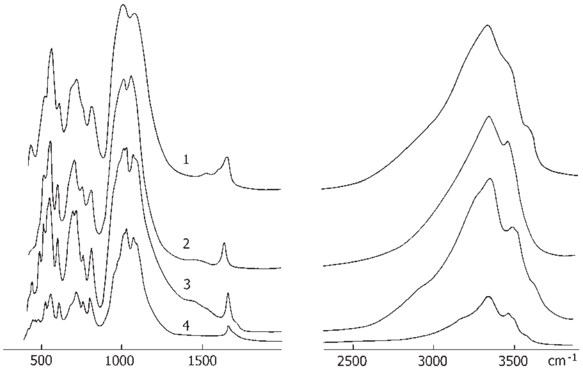

FIGURE 2. IR-spectra of 2005-061 (1), greifensteinite (2), atencioite (3), and footemineite (4).

Footemineite is dimorphous with roscherite, and isostructural with atencioite, a triclinic roscherite-group mineral (Table 7, Fig. 4). It has the same vacant D2 octahedron located at the center of symmetry with coordinates (0.5 0 0), as in atencioite. The site D1 is located at another center of symmetry with coordinates (000) and contains 22.5 electrons. It can correspond to the population $Mn_{0.90}\square_{0.10}$. Nevertheless taking into account that B_{eq} for D1 is 1.86, i.e., a little higher than for M1 and M2, we can suppose that D1 contains admixture of a lighter element. If all Mg is concentrated in D1, so 22.5 electrons can correspond to the population $Mn_{0.88}Mg_{0.05}\square_{0.07}$. Maximum possible Li content in the D1 site corresponds to the composition $Mn_{0.89}Li_{0.11}\square_{0.06}$. This composition is improbable because site thermal parameters indicate that most part of Li is concentrated in the D2 site. For the D2 site, the displacement parameter B_{iso} is 4.2 indicating predominance of a light cation.

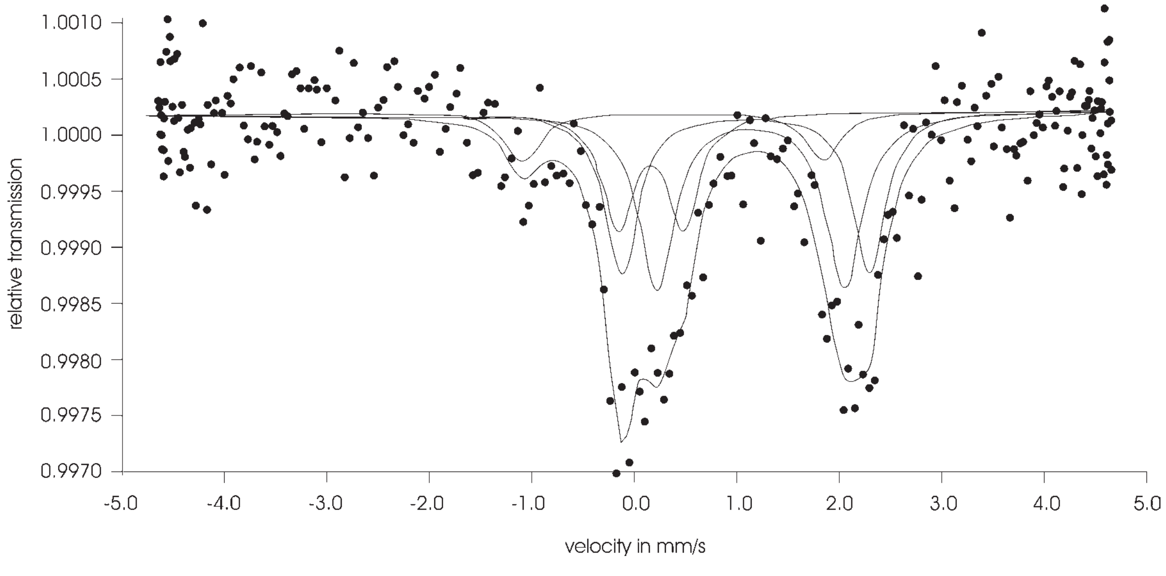

FIGURE 3. Mössbauer spectrum of footemineite.

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[1] Deposit AM-08-001, Table 6. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

Table 1. Chemical data for footemineite

Constituent	wt%	Range	Probe standard
Li_2O	0.23		
BeO	9.54		
CaO	9.43	9.29–9.52	wollastonite
SrO	0.23	n.d.–0.68	SrF_2
BaO	0.24	n.d.–0.38	$BaSO_4$
MgO	0.18	0.08–0.27	diopside
MnO	26.16	25.58–26.80	$MnTiO_3$
FeO*	2.77		Fe
Fe_2O_3*	0.62		Fe
Al_2O_3	0.14	n.d.–0.26	Al_2O_3
P_2O_5	36.58	35.72–37.16	$LaPO_4$
SiO_2	0.42	n.d.–0.83	SiO_2
H_2O	13.1(2)		
Total	99.64		

* Fe total measured as FeO 3.33, range 2.62–4.01.

It contains 1.1 electrons that could correspond to $\square_{0.81}Mg_{0.09}$. But Mg content in the empirical formula is only 0.05 apfu. Therefore we can conclude that D2 concentrates mainly Li. The site D2 contains 1.1 electrons that could correspond, e.g., to the site population $\square_{0.78}Li_{0.17}Mg_{0.05}$ or $\square_{0.95}Mn_{0.05}$. The variant with Li + Mg seems more probable because for this site the displacement parameter is rather high. B_{eq} for this site was not calculated due to its low occupancy. In conclusion, ideally, D1 contains $Mn_{0.90}$ with possible admixture of a light cation. D2 is strongly (>>50%) vacant, but selectively concentrates Li. The presence of Li atoms is unusual for minerals of roscherite group. The bond-valence balance for the site labeled "(OH,H_2O)" is more preferable in the case of its coordination by Mn + Li + Ca (1.54) than in the case of Mn + Mn + Ca (2.26) and allows occupation of neighboring D1 and D2 sites simultaneously in the same unit cell. Therefore the total number of octahedral (M+D) cations could be slightly more than 5. Different occupation of D1 and D2 sites is the main reason for symmetry lowering. Local situations at the junction of two D octahedra in footemineite are listed in Table 8.

Single-crystal X-ray studies (Fanfani et al. 1977) on identical material from the same locality gave the following data (centered unit cell to compare the close lattice analogies of the monoclinic and triclinic roscherite-group minerals): Triclinic, space group: $C\bar{1}$, a = 15.921(5), b = 11.965(4), c = 6.741(1) Å, α = 91.07(8), β = 94.35(8), γ = 89.99(8)°, V = 1280.2 Å^3, Z = 2.

Crystal chemistry of the roscherite group

The roscherite-group minerals can be subdivided into two sub-groups according to symmetry. Most of the investigated samples are monoclinic, space group $C2/c$ (Fanfani et al. 1975; Chukanov et al. 2002, 2007; Rastsvetaeva et al. 2002, 2004a, 2005; Barinova et al. 2004; Atencio et al. 2005). They have a 3D heteropolyhedral framework formed by chains of corner-sharing PO_4 and BeO_4 tetrahedra extending in the [101] direction, which are linked by edge-sharing chains of MO_6 octahedra (M = Mg, Mn, Fe, Al, Zn) parallel to [110] and [1$\bar{1}$0]. Ca^{2+} cations (with sevenfold coordination) and water molecules occupy cavities within the framework. The general crystal-chemical formula of monoclinic roscherite-group minerals can be written as $Ca_2D_2M_4Be_4(PO_4)_6(OH)_4X_2·4H_2O$, where D and M are octahedral sites occupied by Mg, Mn^{2+}, Fe^{2+}, Fe^{3+}, Zn, and Al (all these cations except Al are known as components dominant in M). The D sites are essentially vacant, their common occupancy usually being 1/3 to 1/2 per formula unit. X = OH or H_2O.

In the framework, two PO_4 tetrahedra and two BeO_4 tetrahedra form four-membered rings. Those rings are connected together by additional PO_4 tetrahedra into chains parallel to the [100] direction. D-octahedra, connected via common X-vertices, form chains stretched perpendicular to the twofold axis, i.e., along the short period c ~ 7 Å. These vertices-connected octahedral chains link pairs of edge-connected M-octahedra between them into columns stretched along the [110] direction. Tetrahedral and octahedral constructions are linked together by P-O-M(D) and Be-OH-M bridges, thus forming the three-dimensional framework.

The X site is common for two D-octahedra and one $CaO_4(H_2O)_2X$ polyhedron, and it is located on the twofold axis. Its composition depends on the composition of the D site (Chukanov et al. 2006, their Table 8). Statistically the most probable case is the situation when one of two adjacent D sites is occupied and

Table 2. X-ray powder-diffraction data for footemineite

I_{obs}	d_{obs}	d_{calc}	h	k	l
53	9.575	9.575	0	1	0
3	7.988	7.988	0	1	1
100*	5.998	6.000	0	$\bar{1}$	1
26	4.848	4.852	0	2	1
8	3.369	3.379	1	$\bar{2}$	1
		3.349	$\bar{1}$	$\bar{2}$	1
44	3.192	3.212	2	1	0
5	3.115	3.120	$\bar{2}$	0	1
13	3.072	3.078	0	3	2
14*	3.003	3.000	0	$\bar{2}$	2
38	2.803	2.814	$\bar{1}$	0	3
29	2.650	2.675	$\bar{2}$	0	2
14	2.424	2.427	2	3	1
4	2.393	2.394	0	4	0
8	2.369	2.374	0	$\bar{2}$	3
		2.373	0	$\bar{3}$	2
6	2.267	2.277	$\bar{2}$	1	3
8	2.226	2.227	$\bar{1}$	2	4
		2.226	$\bar{1}$	$\bar{3}$	2
10	1.995	2.000	$\bar{3}$	2	1
		1.992	3	$\bar{1}$	2
6	1.934	1.934	$\bar{2}$	1	4
		1.934	1	$\bar{3}$	3
		1.933	2	$\bar{4}$	0
6	1.657				
5	1.616				

Note: The eight more intense reflections are in bold.
* Preferred orientation due to cleavage.

Table 3. Atomic coordinates and equivalent anisotropic displacement parameters of footemineite (B_{eq}) (standard deviations are given in parentheses)

Site	x/a	y/b	z/c	B_{eq} (Å^2)
Ca	0.7463(2)	0.2608(1)	0.7372(1)	1.30(4)
D1*	0	0	0	1.86(5)
D2*	0.5	0	0	4.2(7)$_{iso}$
M1	0.4924(2)	0.9916(1)	0.6673(1)	1.17(3)
M2	−0.0009(2)	0.6702(1)	0.9877(1)	1.20(3)
P1	0.2465(3)	0.2740(2)	0.7218(2)	1.12(4)
P2	0.4818(3)	0.6931(2)	0.9352(2)	1.14(5)
P3	−0.0249(3)	0.9360(2)	0.6947(2)	1.07(5)
Be1	0.697(2)	0.506(1)	0.157(1)	1.3(3)
Be2	0.796(2)	0.841(1)	0.495(1)	1.3(2)
O1	0.1953(8)	0.9555(5)	0.3260(5)	1.3(1)
O2	0.6954(8)	0.3281(5)	0.9555(5)	1.4(1)
O3	0.4513(8)	0.6185(5)	0.8218(5)	1.3(1)
O4	0.3269(8)	0.3673(5)	0.9918(5)	1.4(1)
O5	0.6742(9)	0.5813(6)	0.2846(5)	1.7(1)
O6	0.4205(8)	0.1690(5)	0.7505(5)	1.3(1)
O7	0.0737(8)	0.2288(5)	0.8365(5)	1.4(1)
O8	0.5091(8)	0.8500(5)	0.8673(5)	1.4(1)
O9	0.1699(8)	0.0091(5)	0.6257(6)	1.3(1)
O10	0.1627(8)	0.2838(5)	0.5797(5)	1.4(1)
O11	0.9369(8)	0.8186(5)	0.6281(5)	1.2(1)
O12	−0.0057(8)	0.1255(6)	0.1490(5)	1.5(1)
OH1	0.5632(8)	0.8572(5)	0.5396(5)	1.4(1)
OH2	0.9312(8)	0.4649(5)	0.1391(5)	1.3(1)
(OH,H_2O)	0.7131(7)	0.0443(5)	0.9543(5)	1.8(1)
H_2O1	0.2228(7)	0.4887(5)	0.3263(5)	1.9(1)
H_2O2	0.2648(7)	0.6724(5)	0.5170(5)	1.9(1)

Note: Approximation of O atoms by hydroxyl groups and water molecules made on basis of charge balance.
* Occupancies of D1 and D2 are 0.9 and 0.22, respectively.

TABLE 4. Selected bond lengths (Å) for footemineite

Ca-O1	2.418(6)
Ca-O2	2.454(6)
Ca-O6	2.410(6)
Ca-O7	2.479(5)
Ca-(OH,H_2O)	2.605(4)
Ca-H_2O1	2.415(5)
Ca-H_2O2	2.451(5)
Mean	2.462
D1-O7	2.454(5) ×2
D1-O12	2.194(6) ×2
D1-(OH,H_2O)	2.037(5) ×2
Mean	2.228
D2-O6	2.677(5) ×2
D2-O8	2.256(6) ×2
D2-(OH,H_2O)	1.527(4) ×2
Mean	2.153
M1-O1	2.217(6)
M1-O6	2.176(6)
M1-O8	2.113(5)
M1-O9	2.251(5)
M1-OH1	2.112(6)
M1-OH1′	2.246(5)
Mean	2.186
M2-O2	2.196(6)
M2-O4	2.244(6)
M2-O7	2.271(6)
M2-O12	2.114(5)
M2-OH2	2.109(6)
M2-OH2′	2.223(5)
Mean	2.193
P1-O5	1.545(6)
P1-O6	1.533(5)
P1-O7	1.561(5)
P1-O10	1.552(6)
Mean	1.548
P2-O2	1.539(5)
P2-O3	1.551(6)
P2-O4	1.556(6)
P2-O8	1.535(5)
Mean	1.545
P3-O1	1.533(5)
P3-O9	1.553(5)
P3-O11	1.540(6)
P3-O12	1.541(5)
Mean	1.542
Be1-O3	1.59(1)
Be1-O4	1.67(1)
Be1-O5	1.64(1)
Be1-OH2	1.63(1)
Mean	1.63
Be2-O9	1.65(1)
Be2-O10	1.62(1)
Be2-O11	1.65(1)
Be2-OH1	1.62(1)
Mean	1.64

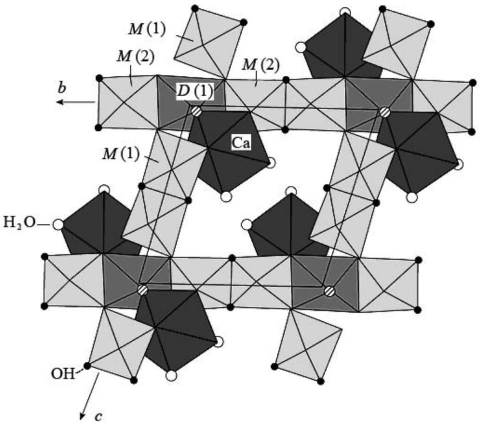

FIGURE 4. Crystal structure of footemineite. D2 octahedron not shown due its low occupancy.

another is vacant. For this reason, the probability of the presence of O atom in the *X* site is low.

In all structurally investigated monoclinic roscherite-group minerals, mean cation-anion distances in D site are greater than that in the M site. This comparison shows that D site is more preferable for occupation by larger bivalent cations than by smaller cations like Fe^{3+} or Al^{3+}. In the first structural investigation of zanazziite (Fanfani et al. 1975), $Al_{2/3}$ was put in the D site. But later Fanfani et al. (1977) stated that "considerations on the atomic arrangement do not exclude the possibility of roscherites where the octahedral trivalent sites are partially or completely occupied by divalent cations… This series would belong to the monoclinic system" (p. 177–178). Fanfani et al. (1977) suggested the following idealized formula for a partly vacant (in the D site) roscherite-group mineral: $Ca_2(Me^{2+}_1\square_1)Me^{2+}_4Be_4(PO_4)_6(OH)_4{\cdot}6H_2O$. Moreover, as it was shown later by Leavens et al. (1990), the investigated sample actually contains <1/3 apfu Al. Taking into account that Fe^{3+} and Al^{3+} are smaller than Mg^{2+}, the authors of this work placed them in the M site, whereas for the D site they give the composition $Mg_{0.61}Fe_{0.40}\square_{0.99}$. The ideal formula for zanazziite is (Leavens et al. 1990) $Ca_2Me^{2+}Me^{2+}_4Be_4(PO_4)_6(OH)_4{\cdot}6H_2O$ where Me^{2+} indicates divalent Mg, Fe, and Mn, with Mg > Fe and Mg > Mn.

TABLE 5. Valence balance* for footemineite

Anion/cation	Ca	D1	D2	M1	M2	P1	P2	P3	Be1	Be2	Σ
O1	0.30			0.29				1.26			1.85
O2	0.27				0.31		1.24				1.82
O3							1.20		0.57		1.77
O4					0.27		1.18		0.46		1.91
O5						1.22			0.50		1.72
O6	0.30		0.01 ×2	0.33		1.26					1.90
O7	0.25	0.15 ×2			0.25	1.16					1.81
O8			0.03 ×2	0.39			1.25				1.67
O9				0.27				1.19		0.48	1.94
O10						1.19				0.52	1.71
O11								1.23		0.48	1.71
O12		0.30 ×2			0.39			1.23			1.92
OH1				0.39, 0.27						0.52	1.18
OH2					0.39, 0.29				0.51		1.19
OH,H_2O	0.18	0.46 ×2	0.22 ×2								0.86
H_2O1	0.30										0.30
H_2O2	0.27										0.27
Σ	1.87	1.82	0.52	1.94	1.90	4.83	4.87	4.91	2.04	2.00	

* Calculated from Brown and Altermatt (1985); valence balances are in v.u. (valence units).

TABLE 7. Comparative data for roscherite, footemineite, and atencioite

	Roscherite*	Footemineite†	Atencioite‡
Chemical formula	$Ca_2Mn_5Be_4(PO_4)_6(OH)_4·6H_2O$	$Ca_2Mn^{2+}\square Mn^{2+}_2Mn^{2+}_2Be_4(PO_4)_6(OH)_4·6H_2O$	$Ca_2Fe^{2+}\square Mg_2Fe^{2+}_2Be_4(PO_4)_6(OH)_4·6H_2O$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
Unit-cell parameters	*a* 15.935(5), *b* 11.963(3), *c* 6.664(1) Å; β 94.77(2)°	*a* 6.788(2), *b* 9.972(3), *c* 10.014(2) Å; α 73.84(2), β 85.34(2), γ 87.44(2)°	*a* 6.668(1), *b* 9.897(2), *c* 9.883(1) Å; α 73.53(1), β 85.60(1), γ 86.93(1)°
Optical data	n_α 1.624, n_β 1.639, n_γ 1.643, $2V_{calc}$ 54°	n_α 1.620(2), n_β 1.627(2), n_γ 1.634(2), $2V_{obs}$ 80°, $2V_{calc}$ 89.6°	n_α 1.613(2), n_β 1.620(2), n_γ 1.626(2), $2V_{obs}$ 60(10)°, $2V_{calc}$ 85°

* Rastsvetaeva et al. (2005); Larsen and Berman (1934).
† This work.
‡ Chukanov and Möckel (2005); Chukanov et al. (2006).

TABLE 8. Possible local situations at the junction of two D octahedra in footemineite

D1 + D2	*X*
$\square$	H_2O
$\square$ + Li	H_2O
Mn + $\square$	OH
Mn + Li	OH
Mn + Mg	O

In accordance with single-crystal structural data for other monoclinic roscherite-group minerals, D site is 50–67% vacant. As it was demonstrated on the basis of comparative analysis of multiple structures based on heteropolyhedral frameworks (Chukanov and Pekov 2005), M cations (i.e., cations with charges >2, ionic radii 0.6–0.7 Å and coordination number 6) like Al, Fe^{3+} or Mn^{3+} usually do not occupy sites that tend to be vacant, whereas for sites occupied only by D cations (like Mg, Zn, Fe^{2+} or Mn^{2+}) vacancies are typical.

Other roscherite-group minerals are triclinic, space group $C\bar{1}$ or $P\bar{1}$ (Fanfani et al. 1977; Leavens et al. 1990; Taucher et al. 1992; Rastsvetaeva et al. 2004b; Chukanov and Möckel 2005; Chukanov et al. 2006). Crystal structures of these minerals are topologically similar to the structures of their monoclinic analogs. The lowering in symmetry is related to subdividing the D and M sites into pairs of non-equivalent sites occupied by different cations. The general crystal-chemical formula of triclinic roscherite-group minerals can be written as $Ca_2D1D2M1_2M2_2Be_4(PO_4)_6(OH)_4X_2·4H_2O$. As compared with monoclinic analogs, in these minerals the number of independent sites for phosphorus increases from 2 to 3, for beryllium—from 1 to 2; for OH groups linking together M-octahedra and Be-tetrahedra—from 1 to 2; for H_2O molecules coordinating Ca—from 1 to 2. Both sites D1 and D2 preserve the tendency to be vacant; their total occupancy is <50%. Actually, one of the D sites is filled in footemineite and atencioite, and this feature justifies the lowering of symmetry.

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