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GEOCHEMISTRY

The Crystal Structure of Footemineite

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Roscherite, ta manganese and calcium beryllophosphate found in the Greifenstein deposit (Germany), was first described in [1, 2] as a monoclinic mineral (sp. gr. C2/c) with the formula $(Ca,Mn,Fe)_3Be_3(PO_4)_3 \cdot 2H_2O$. Using samples from this deposit, we studied the crystal structure of roscherite [3] and its Fe^{2+}-rich analogue [4]. The latter mineral was approved as greifensteinite by the Commission on New Minerals and Mineral Names of International Mineralogical Association (CNMMN IMA) [5]. Both roscherite and greifensteinite are isostructural with their Mg-rich analogue zanazziite from the Lavra da Ilha deposit (Minas Gerais, Brazil) [6, 7] and with the Zn-bearing variety of zanazziite [8]. The Fe-dominant (IMA No. 2005-061) and Zn-dominant (IMA No. 2006-028) monoclinic members of the roscherite group were recently approved by the CNMMN IMA as new minerals. The absence of large single crystals prevented structural study of the two latter minerals.

The study of a Mn-rich sample from the Foote Mine deposit (California, United States) revealed that roscherite occurs as both monoclinic and triclinic (sp. gr. $C\bar{1}$) modifications [9]. We found atencioite (Fe^{2+},Mg-ordered triclinic mineral of this group) [10, 11], while the triclinic analogue of roscherite (Mn-rich variety) was approved by the CNMMN IMA and named footemineite after the locality of its finding (IMA No. 2006-029). Thus, now the roscherite group includes five monoclinic minerals (roscherite, zanazziite, greifensteinite, mineral IMA No. 2005-061, and mineral IMA No. 2006-028), which differ in the predominant octahedral cation, and two triclinic minerals (atencioite and footemineite). This work is devoted to repeated study of the crystal structure of footemineite in the holotype sample.

Footemineite is enriched in Mn, dimorphous with roscherite, and isostructural with atencioite. The chemical composition of the mineral determined by the EDS and SAED method yields the following empirical formula:

$$(Ca_{1.92}Sr_{0.08})\,(Mn_{4.17}Fe^{2+}_{0.64}\,Li_{0.17}Mg_{0.05})\,Be_4[(PO_4)_{5.83}(SiO_4)_{0.17}](H_2O,OH)_{10}.$$

The presence of significant amounts of trivalent Fe in footemineite inferred in [9] was not confirmed. Based on the Mössbauer spectroscopy data, the Fe^{3+} content does not exceed 0.10–0.15 apf.u.

Diffraction patterns were recorded on the fragment of the platy single crystal (the crystal structural characteristics and experimental conditions are given in Table 1). The parameters of the triclinic unit cell were obtained and refined using an Xcalibur CCD diffractometer. They are linked with the monoclinic cell of other minerals of this group by the transitional matrix [011/01-1/-100] and are close to the unit cell parameters of triclinic roscherite in the base-centered lattice $C\bar{1}$ [9]: $a = 15.978(2)$, $b = 12.006(3)$, $c = 6.788(2)$ Å, $\alpha = 88.24°$, $\beta = 94.52°$, and $\gamma = 90.25°$.

The coordinates of the atencioite structure were used to refine the structure [11]. At an R-factor of 0.067, we calculated the difference factor and localized the octahedral site (1/2 0 0) with weak occupancy (0.1) by a light atom (supposedly, Li). In contrast, this site is vacant in the previously studied triclinic roscherite [9]. Taking into consideration the absorption (based on the DIABS program), as well as the anisotropy of thermal vibrations and extinction ($E = -0.0001129$), the R-fac-

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Table 1. Characteristics of crystals and experimental conditions

a, Å; α	6.788(2); 73.84(2)
b, Å; β	9.972(3); 85.34(2)
c, Å; γ	10.014(2); 87.44(2)
V, $Å^3$	648.74
Crystal size, mm	0.16 × 0.14 × 0.03
Space grou; *Z*	$P\bar{1}$; 2
Radiation; λ, Å	MoK_α; 0.71073
Calculated density ρ, g/cm^3	2.94
Crystal size, mm	0.1 × 0.15 × 0.25
Diffractometer	Xcalibur, CCD-detector
Region of record	$-10 < h < 10$ $-13 < k < 17$ $-15 < l < 18$
Sinθ/λ	<0.95
Total number of reflections	3094 $F > 2\sigma(F)$
Number of independent reflections	1273 $F > 2\sigma(F)$
R factor of averaging equivalent reflections	0.029
R-factor of anisotropic refinement	0.035
Refinement program	AREN [12]
Program for absorption correction	DIFABS [13]

tor decreased to 0.035. The position and equivalent thermal parameters of atoms corresponding to this *R* factor are given in Table 2, while the interatomic distances are given in Table 3.

The minerals of the roscherite group with a general formula $Ca_2D_2M_4Be_4(PO_4)_6X_4 \cdot 6H_2O$ have a 3D structure consisting of tetrahedra and octahedra. The Be and P tetrahedra form infinite chains linked in a mixed framework by *M*-octahedra, which, in turn, are linked by edges in octahedral columns. The framework cavities contain Ca-heptahedra. In the monoclinic minerals, the axial *D*-octahedra are characterized by high occupancy (from 1/3 to 1/2). The triclinic modifications are distinguished from monoclinic ones by the following feature: four (in group $P\bar{1}$, two *D*-octahedra included) instead of two octahedra become independent owing to cation ordering (figure). In the triclinic cell of footemineite, both *D*-octahedra with central sites in {000} and {1/2 0 0} are partly occupied, resulting in a decrease in the total content of octahedral cations (like in the monoclinic modifications) to less than 6.

The minerals of the roscherite group from different deposits have steady compositions of tetrahedral sites but different contents of cations in octahedral sites (Table 4). In particular, zanazziite is dominated by Mg; roscherite, by Mn; and greifensteinite, by Fe^{2+}. At a

Table 2. Coordinates of atoms and equivalent (B_{equiv}) parameters of atomic shifts

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{equiv}, $Å^2$
Ca	0.7463(2)	0.2608(1)	0.7372(1)	1.30(4)
D(1)	0	0	0	1.64(5)*
D(2)	0.5	0	0	$4.2(7)_{iso}$
M(1)	0.4924(2)	0.9916(1)	0.6673(1)	1.17(3)
M(2)	−0.0009(2)	0.6702(1)	0.9877(1)	1.20(3)
P(1)	0.2465(3)	0.2740(2)	0.7218(2)	1.12(4)
P(2)	0.4818(3)	0.6931(2)	0.9352(2)	1.14(5)
P(3)	−0.0249(3)	0.9360(2)	0.6947(2)	1.07(5)
Be(1)	0.697(2)	0.506(1)	0.157(1)	1.3(3)
Be(2)	0.796(2)	0.841(1)	0.495(1)	1.3(2)
O(1)	0.1953(8)	0.9555(5)	0.3260(5)	1.3(1)
O(2)	0.6954(8)	0.3281(5)	0.9555(5)	1.4(1)
O(3)	0.4513(8)	0.6185(5)	0.8218(5)	1.3(1)
O(4)	0.3269(8)	0.3673(5)	0.9918(5)	1.4(1)
O(5)	0.6742(9)	0.5813(6)	0.2846(5)	1.7(1)
O(6)	0.4205(8)	0.1690(5)	0.7505(5)	1.3(1)
O(7)	0.0737(8)	0.2288(5)	0.8365(5)	1.4(1)
O(8)	0.5091(8)	0.8500(5)	0.8673(5)	1.4(1)
O(9)	0.1699(8)	0.0091(5)	0.6257(6)	1.3(1)
O(10)	0.1627(8)	0.2838(5)	0.5797(5)	1.4(1)
O(11)	0.9369(8)	0.8186(5)	0.6281(5)	1.2(1)
O(12)	−0.0057(8)	0.1255(6)	0.1490(5)	1.5(1)
OH(1)	0.5632(8)	0.8572(5)	0.5396(5)	1.4(1)
OH(2)	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_2O(1)	0.2228(7)	0.4887(5)	0.3263(5)	1.9(1)
H_2O(2)	0.2648(7)	0.6724(5)	0.5170(5)	1.9(1)

Note: Occupancy of sites *D*(1) and *D*(2) corresponds to 0.9 and 0.221, respectively.
* B_{iso}.

Table 3. Characteristics of coordination polyhedra of cations

Site	CN	Cation–anion distance, Å		
		min	max	av
Ca	7	2.410(6)	2.605(4)	2.46
D(1)	6	1.527(4)	2.677(5)	2.17
D(2)	6	2.037(5)	2.454(5)	2.23
M(1)	6	2.112(6)	2.251(5)	2.19
M(2)	6	2.109(6)	2.271(6)	2.19
P(1)	4	1.533(5)	1.561(5)	1.55
P(2)	4	1.535(5)	1.556(6)	1.55
P(3)	4	1.533(5)	1.553(5)	1.54
Be(1)	4	1.59(1)	1.67(1)	1.63
Be(2)	4	1.62(1)	1.65(1)	1.64

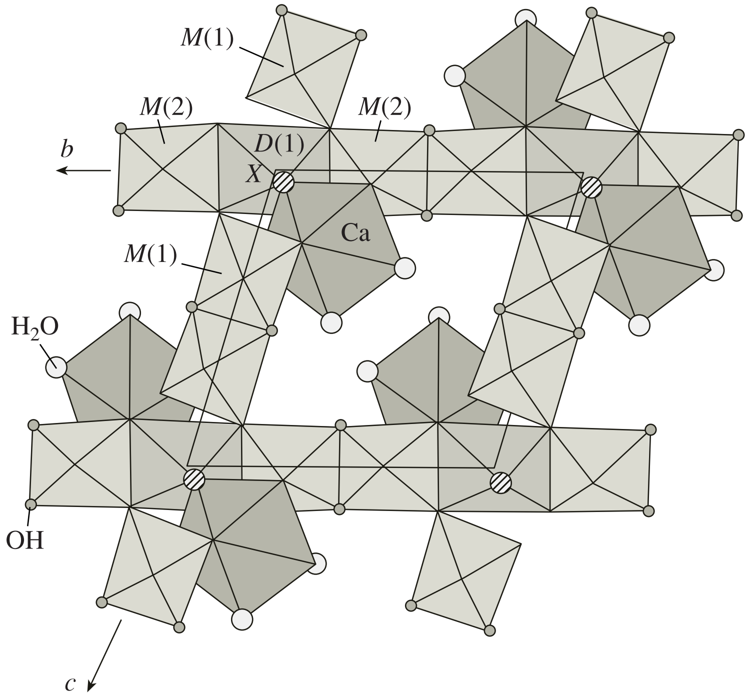
Note: Composition of sites: *D*(1) = 0.9Mn; *D*(2) = 0.17Li + 0.05Mg; *M*(1) = *M*(2) = 2Mn.

Table 4. Crystal structural data on the structurally studied minerals of the roscherite group

Mineral name	Unit cell parameters, Å, degree	Sp. gr.	Distribution of cations over octahedral positions *D* and *M*	Mn : Fe : Mg	Reference
Roscherite	$a = 15.935$, $b = 11.963$, $c = 6.664$ $\beta = 94.77$	*C*2/*c*	$[Al_{0.46}Fe^{2+}_{0.3}Mg_{0.17}\eta_{1.07}][Mn^{2+}_{2.55}Fe^{2+}_{1.45}]$	0.54 : 0.42 : 0.04	[3]
Zanazziite	$a = 15.874$, $b = 11.854$, $c = 6.605$ $\beta = 95.21$	*C*2/*c*	$[Mg_{1.01}\eta_{0.99}][Mg_{2.38}Fe^{2+}_{1.08}Al_{0.31}Mn_{0.2}$ $Fe^{3+}_{0.1}]$	0.05 : 0.25 : 0.71	[7]
Greifensteinite	$a = 15.903$, $b = 11.885$, $c = 6.677$ $\beta = 94.68$	*C*2/*c*	$[Mn^{2+}_{0.7}\eta_{1.3}][(Fe^{2+}, Fe^{3+})_{3.2}Mg_{0.4}Al_{0.4}]$	0.16 : 0.74 : 0.09	[4]
Zn-bearing greifensteinite	$a = 15.941$, $b = 11.877$, $c = 6.625$ $\beta = 95.09$	*C*2/*c*	$[Mn^{2+}_{0.68}\eta_{1.32}]$ $[(Fe^{2+}, Fe^{3+})_{2.35}Zn_{0.72}Mn_{0.46}Al_{0.28}Mg_{0.19}]$	0.31 : 0.64 : 0.05	[8]
Atencioite	$a = 9.883$, $b = 9.879$, $c = 6.668$ $\alpha = 86.93$, $\beta = 85.60$, $\gamma = 73.53$	$P\bar{1}$	$[Fe^{2+}_{0.5}Mn_{0.2}Al_{0.1}\eta_{0.2}][Mg_{0.2}\eta_{0.8}]$ $[Mg_{1.1}Fe^{3+}_{0.5}Fe^{2+}_{0.4}][Fe^{2+}_{1.1}Mg_{0.9}]$	0.04 : 0.51 : 0.45	[11]
Footemineite	$a = 10.014$, $b = 9.972$, $c = 6.788$ $\alpha = 87.44$, $\beta = 85.34$, $\gamma = 73.84$	$P\bar{1}$	$[(Mn, Fe)_{0.9}\eta_{0.1}][Li_{0.17}Mg_{0.05}\eta_{0.78}]$ $[Mn_2][Mn_2]$	0.98 : 0 : 0.02	[Present paper]

Note: For unification, the *a* and *c* parameters of the triclinic cells of atencioite and footemineite are transposed.

homogenous composition (the major cation Mn is insignificantly replaced by the bivalent Fe), the degradation of footemineite symmetry is caused by the ordering of Mn(Fe) and a vacancy in two conjugated *D*-octahedra around inversion centers rather than the ordering of octahedral cations.



Fragment of the footemineite structure consisting of *M*,*D*-octahedra and Ca-polyhedra. *D*(2) octahedron is not shown owing to weak occupancy of the central site.

The crystallochemical formula of footemineite can be presented as follows ($Z = 1$):

$$\mathrm{Ca_2[(Mn,Fe)_{0.9}\square_{0.1}][Li_{0.17}Mg_{0.05}\square_{0.78}][Mn_2][Mn_2]Be_4(PO_4)_6(OH)_4(H_2O)_6},$$

where brackets mark out the compositions of independent octahedral sites.

Thus, the studied mineral differs from other minerals of the roscherite group in the predominance and ordered allocation of Mn in the *M*-octahedral sites, as well as in the presence of vacancies in two *D*-sites, which leads to degradation of the crystal symmetry and transition into a primitive triclinic cell.

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