

CHEMISTRY

# Crystal Structure of a Magnesium-Rich Triclinic Analogue of Greifensteinite

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Presented by Academician L.N. Kogarko April 20, 2004

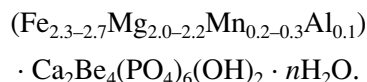
Received April 27, 2004

The beryllium phosphate roscherite from the Greifenstein deposit (Saxony, Germany) was first described as the monoclinic mineral (space group  $C2/c$ )  $(Ca, Mn, Fe)_3Be_3(PO_4)_3 \cdot 2H_2O$  [1, 2]. Later, a magnesia-rich analogue of this mineral from the Lavra da Ilha deposit (Minas Gerais, Brazil) was studied by X-ray diffraction [3, 4]. A study of a manganese-rich specimen from the Foote Mine deposit (California, United States) has shown that a triclinic roscherite modification (space group  $C\bar{1}$ ) exists in addition to the monoclinic one [5]. Recently, the  $Fe^{2+}$ -dominant analogue of roscherite from the Greifenstein deposit has been considered and approved by the Commission on New Minerals and Mineral Names under the name greifensteinite. Thus, the roscherite group currently includes three isostructural minerals, roscherite, zanazziite, and greifensteinite, which differ in the predominant octahedral cations, and the triclinic analogue of roscherite.

Soon after the first publication dealing with the discovery of greifensteinite, the authors found its analogues in some other deposits, including a mine in the vicinity of Galileia (Minas, Gerais, Brazil).

A new sample studied in this work differs from greifensteinite studied previously in both the composition (namely, by high magnesium content) and the IR spectrum, in particular, splitting of some bands, indicating a possible decrease in the symmetry.

The chemical composition of the mineral was determined by local X-ray spectral analysis and calculated to the empirical formula



The X-ray diffraction data were collected from an irregularly shaped fragment of a single crystal. The crystal data and experiment details are summarized in Table 1. The triclinic unit cell parameters were determined and refined on a Kuma-4 CCD diffractometer. They are related to the monoclinic cells of other representatives of this group through the 011/01–1/–100 transition matrix and are close to the parameters of triclinic roscherite

**Table 1.** Crystal data and experiment details

General chemical formula	$(Fe, Mg)_5Ca_2Be_4(PO_4)_6(OH)_4 \cdot 6H_2O$
Unit cell parameters, Å, deg	$a = 6.668(1)$ $\alpha = 73.53(1)$ $b = 9.879(2)$ $\beta = 85.60(1)$ $c = 9.883(1)$ $\gamma = 86.93(1)$
Unit cell volume $V$ , Å <sup>3</sup>	622.06
Space group	$P\bar{1}$
Calculated density $\rho$ , g/cm <sup>3</sup>	2.88
Absorption coefficient $\mu$ , mm <sup>-1</sup>	27.52
Formula weight	1078.2
Diffractometer	Kuma-4 CCD
Radiation; wavelength, Å	MoK $\alpha$ ; 0.71073
Crystal size, mm	0.5 × 0.25 × 0.125
The maximum $\sin\theta/\lambda$ , Å <sup>-1</sup>	0.69
Scan range	$-8 < h < 9$ ; $-12 < k < 13$ ; $-13 < l < 13$
The total number of reflections	6957
The number of independent reflections	1126 $ F  > 3\sigma(F)$
$R_{av}$ for equivalent reflections	0.045
Software for structural calculations	AREN [8]
Absorption corrections	DIFABS [9]
$R_{hkl}$ in the anisotropic approximation	0.051
Extinction parameter $E$	0.0000417

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**Table 2.** Atomic coordinates and equivalent thermal parameters

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> <sub>eq</sub> , Å <sup>2</sup>
Ca	0.7457(2)	0.2605(1)	0.7382(1)	1.18(5)
<i>M</i> (1)	0	0	0	1.39(7)
<i>M</i> (2)	0.5	0	0	1.6(4)
<i>M</i> (3)	0.4925(2)	0.9934(1)	0.6636(1)	1.10(4)
<i>M</i> (4)	-0.0021(2)	0.6674(1)	0.9904(1)	1.33(4)
P(1)	0.2469(3)	0.2703(2)	0.7252(2)	0.91(6)
P(2)	0.4800(3)	0.6962(2)	0.9304(2)	0.88(5)
P(3)	-0.0245(3)	0.9322(2)	0.6973(2)	0.79(5)
Be(1)	0.698(2)	0.513(1)	0.153(1)	1.4(3)
Be(2)	0.808(1)	0.8436(9)	0.494(1)	0.8(2)
O(1)	0.2012(7)	0.9602(5)	0.3264(6)	0.9(1)
O(2)	0.7000(8)	0.3267(5)	0.9591(5)	1.1(2)
O(3)	0.4487(8)	0.6199(6)	0.8173(5)	1.2(1)
O(4)	0.3259(7)	0.3657(5)	0.9937(6)	1.2(1)
O(5)	0.6671(8)	0.5873(6)	0.2810(5)	1.4(2)
O(6)	0.4214(7)	0.1622(5)	0.7539(6)	1.2(1)
O(7)	0.0697(8)	0.2300(6)	0.8409(6)	1.3(1)
O(8)	0.5059(8)	0.8541(5)	0.8596(5)	1.0(2)
O(9)	0.1737(7)	0.0037(5)	0.6309(5)	1.1(1)
O(10)	0.1573(8)	0.2814(5)	0.5848(6)	1.3(2)
O(11)	0.9383(8)	0.8173(5)	0.6263(5)	1.2(1)
O(12)	-0.0004(8)	0.1357(6)	0.1418(6)	1.2(2)
OH(1)	0.5613(8)	0.8630(5)	0.5379(5)	0.9(1)
OH(2)	0.9349(8)	0.4636(6)	0.1370(6)	1.2(2)
(OH, H <sub>2</sub> O)	0.7204(9)	0.0408(5)	0.9571(6)	2.3(1)
H <sub>2</sub> O(1)	0.2189(8)	0.4887(6)	0.3268(6)	1.5(2)
H <sub>2</sub> O(2)	0.274(1)	0.6714(6)	0.5153(6)	2.1(2)
H(1)	-0.194(7)	0.573(6)	-0.415(5)	3*
H(2)	-0.315(8)	0.546(6)	-0.276(6)	3*
H(3)	0.799(8)	0.289(5)	0.454(6)	3*
H(4)	0.767(7)	0.400(5)	0.510(5)	3*

Note: *M*(1) = Fe<sub>0.5</sub><sup>2+</sup>Mn<sub>0.2</sub><sup>2+</sup>Al<sub>0.1</sub>; *M*(2) = Mg<sub>0.2</sub>; *M*(3) = Mg<sub>1.1</sub>Fe<sub>0.5</sub><sup>3+</sup>Fe<sub>0.4</sub><sup>2+</sup>; *M*(4) = Fe<sub>1.1</sub><sup>2+</sup>Mg<sub>0.9</sub>.

\* Isotropic thermal parameters (were not refined).

(in the base-centered system). A set of experimental data was obtained on the same diffractometer.

The set of atomic coordinates of the greifensteinite [7] transformed for the triclinic *P* cell was taken as the initial set for structure refinement. The distribution of cations over three independent octahedral positions was realized using mixed atom scattering curves based

on the known chemical composition and with allowance for crystal chemical criteria such as the ion radius and thermal vibrations of the cations, position populations, and the minimum *R* factors. At the stage of *R* = 5.9%, the difference synthesis was calculated, from which the fourth octahedral position (1/2 0 0) with a low population (0.2 Mg atom) was derived. The H atoms of two water molecules were also located from the difference electron density synthesis. Taking into account the thermal vibration anisotropy reduced the *R* factor to 5.1%. The positional and equivalent thermal parameters of atoms corresponding to this *R* factor are listed in Table 2, while the interatomic distances are given in Table 3.

The structure of the triclinic greifensteinite analogue, like those of other representatives of the roscherite group studied previously, is a three-dimensional structure composed of tetrahedra, octahedra, and Ca seven-vertex polyhedra. The Be and P tetrahedra form infinite chains combined into a mixed framework through *M* octahedra, which, in turn, form octahedral chains by sharing edges (Fig. 1). Calcium occurs in the framework cavities. The octahedra at the cell points are usually partially populated and, hence, the total number of *M* cations is reduced from six to five and the chains are split statistically into pairs of octahedra.

The environment of the *M*(1) polyhedron includes two water molecules at distances of 1.939 Å, while in the case of *M*(2) these distances are 1.549 Å. The shorter distances are due to the very low population of the position by Mg atoms (0.2) and to partial replacement of a water molecule by an OH group. The Ca polyhedron is coordinated by four oxygen atoms and three water molecules, one of these being a part of the environments of the *M*(1) and *M*(2) octahedra.

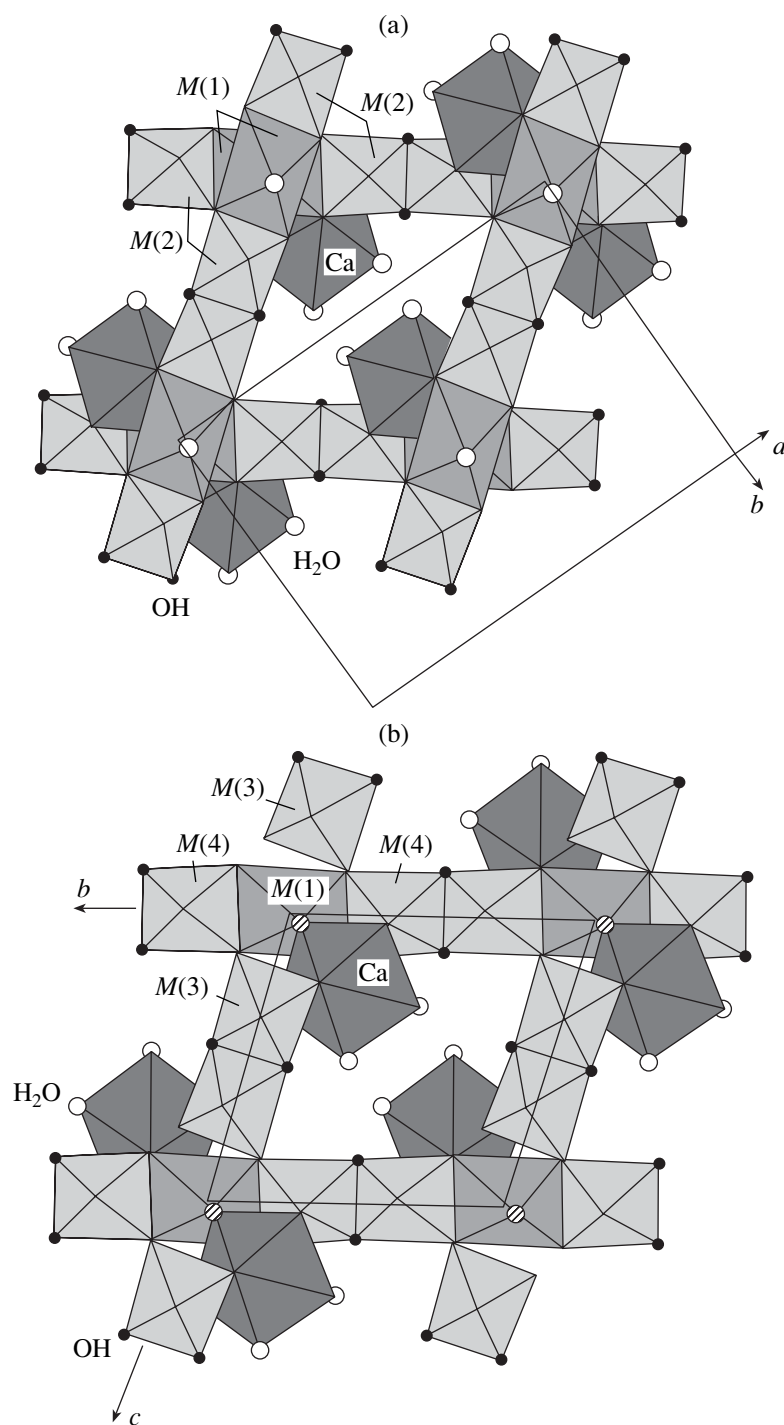
The roscherite-group minerals from different deposits, characterized by an invariable composition in the tetrahedral positions, differ in the contents of cations in the octahedral positions (Table 4). For instance, Mg predominates in zanazziite (three atoms of five), while Mn is the predominant cation in roscherite and Fe predominates in greifensteinite. The difference between the triclinic and monoclinic modifications of greifensteinite is that Mg (2.2 atoms) becomes the partner of iron instead of Mn and some of Fe(II) is replaced by Fe(III). The distribution of these elements, together with the admixture Mn and Al cations, is ordered; therefore, four rather than two octahedral positions become independent; this decreases the crystal symmetry to triclinic and simultaneously distorts the cell (the  $\alpha$  and  $\gamma$  angles are no longer 90°). Therefore, we switched from a triclinic cell with  $C\bar{1}$  symmetry (triclinic roscherite) to a primitive triclinic cell with  $P\bar{1}$  symmetry. Presumably, a higher order would result in a further decrease in symmetry to *P*1 with an increase in the number of independent positions to six.

**Table 3.** Interatomic distances (Å) and angles (deg)

<i>P</i> tetrahedra					
P(1)–O(6)	1.523(5)	P(2)–O(8)	1.530(5)	P(3)–O(1)	1.529(5)
O(10)	1.526(6)	O(2)	1.539(5)	O(11)	1.533(6)
O(5)	1.531(6)	O(3)	1.546(6)	O(9)	1.542(5)
O(7)	1.564(5)	O(4)	1.554(5)	O(12)	1.559(5)
	⟨1.536⟩		⟨1.542⟩		⟨1.541⟩
Be tetrahedra			Ca seven-vertex polyhedron		
Be(1)–O(4)	1.61(1)	Be(2)–O(11)	1.57(1)	Ca–O(6)	2.393(5)
O(3)	1.62(1)	O(10)	1.63(1)	H <sub>2</sub> O(1)	2.397(6)
O(5)	1.63(1)	O(9)	1.66(1)	H <sub>2</sub> O(2)	2.414(6)
OH(2)	1.63(1)	OH(1)	1.68(1)	O(7)	2.425(5)
	⟨1.62⟩		⟨1.64⟩	O(1)	2.440(6)
				O(2)	2.444(6)
				(OH, H <sub>2</sub> O)	2.595(5)
					⟨2.444⟩
<i>M</i> octahedra					
<i>M</i> (1)–(OH, H <sub>2</sub> O)	1.939(6) × 2	<i>M</i> (2)–(OH, H <sub>2</sub> O)	1.549(8) × 2		
O(12)	2.196(6) × 2	O(8)	2.266(8) × 2		
O(7)	2.413(5) × 2	O(6)	2.581(6) × 2		
	⟨2.183⟩		⟨2.132⟩		
<i>M</i> (3)–O(8)	2.038(4)	<i>M</i> (4)–O(12)	2.012(5)		
OH(1)	2.041(6)	OH(2)	2.058(7)		
O(6)	2.120(6)	O(2)	2.119(5)		
O(1)	2.132(5)	OH(2)	2.161(5)		
OH(1)	2.135(5)	O(4)	2.188(5)		
O(9)	2.167(5)	O(7)	2.191(7)		
	⟨2.106⟩		⟨2.122⟩		
H bonds					
H(1)–H <sub>2</sub> O(1)	0.92(1)	H(1)H <sub>2</sub> O(1)H(2)	112.2(7)		
H(2)–H <sub>2</sub> O(1)	0.89(2)	H(3)H <sub>2</sub> O(2)H(4)	115.8(8)		
H(3)–H <sub>2</sub> O(2)	0.71(2)	H <sub>2</sub> O(1)H(1)O(10)	171.5(9)		
H(4)–H <sub>2</sub> O(2)	0.88(1)	H <sub>2</sub> O(1)H(2)O(3)	173.0(1)		
H(1)–H(2)	1.51(1)	H <sub>2</sub> O(2)H(3)O(11)	172.4(9)		
H(3)–H(4)	1.36(1)	H <sub>2</sub> O(2)H(4)O(5)	176.3(8)		
H(1)···O(10)	1.88(1)				
H(2)···O(3)	1.97(2)				
H(3)···O(11)	2.19(2)				
H(4)···O(5)	2.59(1)				

The crystal chemical formula of the mineral can be represented as follows ( $Z = 1$ ):  $[(\text{Fe}_{0.5}^{2+} \text{Mn}_{0.2}^{2+} \text{Al}_{0.1-0.2}) (\text{Mg}_{0.2-0.8}) (\text{Mg}_{1.1} \text{Fe}_{0.5}^{3+} \text{Fe}_{0.4}^{2+}) \cdot (\text{Fe}_{1.1}^{2+} \text{Mg}_{0.9})] \text{Ca}_2 \text{Be}_4 (\text{PO}_4)_6 (\text{OH})_4 (\text{OH}, \text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ , where the compositions of the independent octahedral positions are indicated in brackets.

According to the local valences balance [10], the excess bond valence sum in one H<sub>2</sub>O position indicates partial replacement of this molecule by OH groups, which reduces the total number of H<sub>2</sub>O molecules in the mineral. This replacement accounts for the unsuccessful attempt to locate the H atoms of this water molecule.



**Fig. 1.** Fragment of the greifensteinite structure composed of *M* octahedra and Ca polyhedra in the (a) monoclinic and (b) triclinic cells. Due to the low population of the position, the *M*(2) octahedron in the triclinic cell is not shown.

The H-bond parameters determined for other water molecules (Table 3) indicate a substantial role of hydrogen bonds in the mineral structure.

The distribution of Fe<sup>2+</sup> and Fe<sup>3+</sup> over the positions was done resorting to Mössbauer spectroscopy data, indicating that divalent iron, which makes up 64.2% of the total iron content, occupies one position; another

9.2% of Fe<sup>2+</sup> is in the second position; and 5.8% of Fe<sup>2+</sup> is in the third position. The last two lines have very similar Mössbauer parameters, the differences between them being attributable to local situations (e.g., different ligands or different neighboring cations). Thus, they can be combined into a single position (the third one). The possibility of occasional coincidence of the Fe<sup>2+</sup>

**Table 4.** Crystal data for minerals of the roscherite group from various deposits

Mineral	Unit cell parameters, Å, deg	Space group	Formula	Mn : Fe : Mg	Ref.
Roscherite*	$a = 15.90, b = 11.88,$ $c = 6.69$ $\beta = 94.7$	$C2/c$	$(\text{Mn, Fe})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.85 : 0.14 : 0.01	[2]
Zanazziite	$a = 15.874, b = 11.854,$ $c = 6.605$ $\beta = 95.21$	$C2/c$	$(\text{Mg, Fe})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_{3.4} \cdot 6.6\text{H}_2\text{O}$	0.05 : 0.33 : 0.62	[4]
Greifensteinite	$a = 15.903, b = 11.885,$ $c = 6.677$ $\beta = 94.68$	$C2/c$	$(\text{Fe, Mn})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.16 : 0.74 : 0.09	[7]
Triclinic roscherite	$a = 15.921, b = 11.965,$ $c = 6.741$ $\alpha = 91.04, \beta = 94.21,$ $\gamma = 89.59$	$C\bar{1}$	$(\text{Mn, Fe})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.90 : 0.09 : 0.01	[5]
Triclinic analogue of greifensteinite	$a = 9.883, b = 9.879,$ $c = 6.668$ $\alpha = 86.93, \beta = 85.60,$ $\gamma = 73.53$	$P\bar{1}$	$(\text{Fe, Mg})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.04 : 0.51 : 0.45	[This work]

Note: The  $a$  and  $c$  parameters for the triclinic analogue of greifensteinite are interchanged for uniformity.

\* No structural study has been performed.

Mössbauer lines for the first and the last positions, which make up in total 1.6 of 2.5 iron atoms and correspond to 64%, was also taken into account. The remaining 20.8% of Fe atoms correspond to Fe(III) and occupy one of the above-listed positions, namely, the third one.

The monoclinic minerals of the roscherite group (Fig. 1a) have only one speciating octahedral position, a fourfold one, because the other position (located at a center of inversion) tends to be vacant (greifensteinite) or to contain the same dominating cation as the main one (zanazziite). In the triclinic mineral (Fig. 1b), three positions (apart from the vacancy) are significant for systematization and the idealized formula of the mineral can be written as  $(\text{Fe}^{2+}, \text{Mn})(\text{Mg}, \text{Fe}^{3+})_2(\text{Fe}^{2+}, \text{Mg})_2 \cdot \text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ .

Thus, the mineral we studied differs from other representatives of the roscherite group by a specific combination of elements in the octahedral positions, by their ordered distribution over these positions with a decrease in the crystal symmetry, and by transformation into a triclinic primitive cell.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 02–05–64080) and the program “Leading Scientific Schools” (NSH-1087-2003-5).

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