

# Crystal structure of rimkorolgitite, Ba[Mg<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub>(PO<sub>4</sub>)<sub>4</sub>](H<sub>2</sub>O), and its comparison with bakhchisaraitsevite

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**Abstract:** The crystal structure of rimkorolgitite, ideally Ba[Mg<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub>(PO<sub>4</sub>)<sub>4</sub>](H<sub>2</sub>O), (monoclinic,  $P2_1/c$ ,  $a = 8.3354(9)$ ,  $b = 12.8304(13)$ ,  $c = 18.313(2)$  Å,  $\beta = 90.025(2)^\circ$ ,  $V = 1958.5(4)$  Å<sup>3</sup>,  $Z = 4$ ) has been solved by direct methods and refined to  $R_1 = 0.052$  using X-ray diffraction data collected from a crystal twinned on (001). There are five symmetrically independent Mg<sup>2+</sup> cations that are each octahedrally coordinated by four O atoms and two H<sub>2</sub>O groups. One symmetrically independent Ba<sup>2+</sup> cation is coordinated by eight O atoms and two H<sub>2</sub>O groups. The Mgφ<sub>6</sub> octahedra (φ = O, H<sub>2</sub>O) and PO<sub>4</sub> tetrahedra form sheets parallel to (001). Their main elements are zigzag chains of the Mgφ<sub>6</sub> edge-sharing octahedra. The chains are linked *via* common vertices to form an octahedral sheet in which Mg atoms are located at the vertices of the 6<sup>3</sup> hexagonal net. The PO<sub>4</sub> tetrahedra are above and below hexagonal rings of Mg octahedra and are linked to them by sharing common O vertices. The Ba atoms and H<sub>2</sub>O(1) and H<sub>2</sub>O(22) groups are located between the sheets providing their linkage into three-dimensional structure. The structure of rimkorolgitite is closely related to that of bakhchisaraitsevite, Na<sub>2</sub>Mg<sub>5</sub>(PO<sub>4</sub>)<sub>4</sub>·7H<sub>2</sub>O. Both structures are based on the octahedral-tetrahedral sheets of the same type. In bakhchisaraitsevite, the sheets are linked into three-dimensional framework by edge-sharing between the Mgφ<sub>6</sub> octahedra from two adjacent sheets, whereas in rimkorolgitite, there is no linkage between adjacent sheets. The structure of rimkorolgitite can be considered as bakhchisaraitsevite-like framework interrupted by the presence of large Ba<sup>2+</sup> cations.

**Key-words:** rimkorolgitite, crystal structure, bakhchisaraitsevite.

## Introduction

Rimkorolgitite, BaMg<sub>5</sub>(PO<sub>4</sub>)<sub>4</sub>·8H<sub>2</sub>O, was described by Britvin *et al.* (1995) from dolomitic carbonatites of the Kovdor iron deposits, Kola peninsula, Russia. The mineral occurs as yellowish-brown to dark rose crystals elongated in [010] with a pseudo-hexagonal prismatic habit. The chemical formula of rimkorolgitite corresponds to (Mg<sub>4.84</sub>Mn<sub>0.16</sub>)<sub>Σ5.00</sub>(Ba<sub>0.86</sub>Sr<sub>0.13</sub>Ca<sub>0.01</sub>)<sub>ΔΣ1.00</sub>(PO<sub>4</sub>)<sub>4.00</sub>·8H<sub>2</sub>O or ideally BaMg<sub>5</sub>(PO<sub>4</sub>)<sub>4</sub>·8H<sub>2</sub>O. The mineral was named in honour of Olga Mikhailovna Rimskaya-Korsakova (1914–1987), granddaughter of the famous Russian composer N.A. Rimskiy-Korsakov, due to her important contributions to the mineralogy of Kola alkaline complexes and, in particular, of Kovdor iron deposits (see more details, *e.g.* in Anastasenko & Krivovichev (1998)). Single-crystal precision and Weissenberg studies carried out by Britvin *et al.* (1995) indicated that rimkorolgitite is probably orthorhombic,  $a = 12.8$ ,  $b = 8.35$ ,  $c = 18.4$  Å, with possible space groups  $Pcmm$  or  $Pcm2_1$ .

Recently, Liferovich *et al.* (2000) described a new mineral species, bakhchisaraitsevite, ideally Na<sub>2</sub>Mg<sub>5</sub>(PO<sub>4</sub>)<sub>4</sub>·7H<sub>2</sub>O, from the Kovdor alkaline complex. The crystal-structure determination for bakhchisaraitsevite (Yakubovich *et al.*, 2000) demonstrated that it is monoclinic, space group  $P2_1/c$ , with  $a = 8.324(4)$ ,  $b = 12.926(4)$ ,  $c = 17.519(9)$  Å,  $\beta = 102.03(1)^\circ$ . Note that the  $a$  and  $b$  unit-cell parameters are close to those for rimkorolgitite. The structure of bakhchisaraitsevite consists of a framework of linked Mgφ<sub>6</sub> octahedra (φ = O, H<sub>2</sub>O) and PO<sub>4</sub> tetrahedra, with Na atoms and H<sub>2</sub>O groups located in channels. On the basis of comparison of the unit cells and chemical formulae of rimkorolgitite and bakhchisaraitsevite, Yakubovich *et al.* (2000) proposed that these minerals are structurally related and that the correct symmetry for rimkorolgitite is monoclinic. Below we will show that both these statements are correct.

The purpose of this paper is to describe results of crystal-structure determination of rimkorolgitite and to discuss its relationship to bakhchisaraitsevite.

Table 1. Crystallographic data and refinement parameters for rimkorolite, Ba[Mg<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub>(PO<sub>4</sub>)<sub>4</sub>](H<sub>2</sub>O).

<i>a</i> (Å)	8.3354(9)
<i>b</i> (Å)	12.8304(13)
<i>c</i> (Å)	18.313(2)
$\beta$ (°)	90.025(2)
<i>V</i> (Å <sup>3</sup> )	1958.5(4)
<i>Z</i>	4
Space group	<i>P2<sub>1</sub>/c</i>
<i>F</i> <sub>000</sub>	1536
$\mu$ (cm <sup>-1</sup> )	26.36
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	2.66
Crystal size (mm)	0.20 x 0.07 x 0.05
Radiation	MoK $\alpha$
Total ref.	21507
Unique ref.	7942
Unique $ F_o  \geq 4\sigma_F$	4663
<i>R</i> *	0.052
<i>wR</i>	0.092
<i>S</i>	0.923

\*  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ ;  $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ , for *m* observations and *n* parameters

$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$

## Experimental

### Data collection

The crystals of rimkorolite used in this study were from the holotype specimen described by Britvin *et al.* (1995). An examination of the crystals using a polarizing microscope showed that most of them are subparallel intergrowths of two or three smaller prismatic crystals. A suitable single crystal was mounted on a Bruker three-circle X-ray diffractometer operated at 50 kV and 40 mA and equipped with new CCD APEX area detector. More than a hemisphere of three-dimensional data was collected using monochromatic MoK $\alpha$  X-radiation, with frame widths of 0.3° in  $\omega$ , and with 10 seconds spent counting for each frame. The unit-cell parameters (Table 1) were refined with 1752 reflections using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was done based upon 720 intense reflections. The crystal was modeled as an ellipsoid, which lowered the *R*<sub>int</sub> from 0.033 to 0.029 %.

Table 2. Atomic coordinates and displacement parameters (x 10<sup>4</sup> Å<sup>2</sup>) for rimkorolite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Ba	0.23818(5)	0.08279(3)	0.00270(3)	168(1)	132(2)	169(2)	202(2)	3(2)	-14(3)	9(2)
Mg(1)	-0.2804(3)	0.1866(1)	-0.0681(1)	60(4)	60(10)	51(8)	67(10)	12(7)	12(9)	-11(8)
Mg(2)	0.1951(3)	-0.0758(2)	-0.2292(1)	114(5)	79(11)	85(10)	177(12)	1(9)	1(9)	10(8)
Mg(3)	-0.1979(3)	-0.0817(2)	-0.2458(1)	113(5)	93(11)	94(10)	151(11)	-24(10)	16(8)	-10(8)
Mg(4)	-0.2956(3)	-0.3127(2)	-0.2691(1)	103(5)	93(11)	66(9)	152(12)	-5(8)	-14(9)	-4(8)
Mg(5)	0.3129(3)	-0.3053(2)	-0.2457(1)	93(4)	88(11)	77(9)	115(11)	-9(9)	22(9)	-10(8)
P(1)	-0.0213(2)	0.0941(1)	-0.1470(1)	106(3)	89(8)	95(7)	135(8)	-6(7)	-1(7)	-3(6)
P(2)	-0.0108(2)	-0.2556(1)	-0.1499(1)	97(3)	79(8)	107(7)	104(8)	-3(7)	-3(7)	-12(6)
P(3)	0.4900(2)	-0.0228(1)	0.14849(9)	97(3)	92(8)	84(7)	115(8)	22(6)	3(7)	2(7)
P(4)	0.5125(2)	0.1408(1)	0.3473(1)	105(3)	78(8)	111(7)	126(9)	-5(7)	2(7)	-17(6)
H <sub>2</sub> O(1)	0.3684(7)	0.2150(4)	0.5338(3)	286(14)	340(30)	200(30)	310(30)	20(20)	40(30)	-10(20)
H <sub>2</sub> O(2)	0.2530(7)	-0.4456(3)	-0.1904(2)	126(8)	140(20)	80(20)	160(20)	-30(20)	-10(20)	-10(20)
O(3)	-0.0536(6)	0.0670(3)	-0.0679(3)	169(11)	180(30)	160(30)	170(30)	-10(20)	0(20)	-40(20)
O(4)	-0.0143(8)	-0.0033(3)	-0.1963(2)	106(9)	90(20)	90(20)	140(20)	-60(20)	-30(20)	10(20)
H <sub>2</sub> O(5)	-0.2462(7)	-0.4472(3)	-0.2051(2)	122(8)	120(20)	80(20)	170(20)	0(20)	0(20)	10(20)
O(6)	0.4484(6)	-0.0632(3)	0.0711(3)	100(10)	160(20)	60(20)	70(20)	20(20)	-10(20)	0(20)
O(7)	0.1485(5)	-0.2219(3)	-0.1860(3)	106(9)	70(20)	80(20)	170(20)	-10(20)	50(20)	-30(20)
O(8)	-0.0296(6)	-0.2006(3)	-0.0767(2)	135(10)	140(20)	150(20)	120(20)	-40(20)	40(20)	40(20)
O(9)	0.6452(5)	0.1593(3)	0.2898(3)	110(9)	80(20)	90(20)	150(20)	30(20)	60(20)	-10(20)
O(10)	0.1334(6)	0.1549(3)	-0.1520(3)	178(11)	180(30)	150(20)	210(30)	-20(20)	50(20)	-90(20)
O(11)	-0.1480(6)	-0.2277(3)	-0.2016(3)	131(10)	130(20)	130(20)	130(20)	20(20)	-30(20)	20(20)
H <sub>2</sub> O(12)	0.5126(6)	-0.2630(3)	-0.1749(2)	153(10)	120(20)	160(20)	180(30)	-40(20)	20(20)	10(20)
O(13)	-0.1660(6)	0.1625(3)	-0.1694(3)	142(10)	110(20)	170(20)	150(30)	0(20)	-30(20)	60(20)
O(14)	0.3645(5)	0.0592(3)	0.1697(3)	136(10)	120(20)	60(20)	230(30)	0(20)	60(20)	30(20)
O(15)	0.3499(5)	0.1695(3)	0.3126(2)	106(9)	70(20)	100(20)	150(20)	10(20)	-30(20)	50(20)
O(16)	0.4958(6)	-0.1157(3)	0.2022(2)	110(9)	80(20)	110(20)	140(20)	40(20)	-30(20)	10(20)
O(17)	0.5112(6)	0.0241(3)	0.3700(2)	131(10)	140(20)	50(20)	200(20)	30(20)	20(20)	-40(20)
H <sub>2</sub> O(18)	-0.0050(6)	0.3753(3)	-0.1811(3)	176(11)	170(30)	150(20)	220(30)	0(20)	40(20)	-10(20)
H <sub>2</sub> O(19)	-0.2704(7)	0.1543(4)	0.0388(3)	279(13)	200(30)	390(30)	250(30)	-50(20)	-140(30)	-190(30)
O(20)	0.6568(5)	0.0290(3)	0.1467(3)	132(10)	90(20)	120(20)	180(30)	10(20)	-10(20)	-30(20)
O(21)	-0.0072(6)	-0.3758(3)	-0.1375(2)	134(10)	110(20)	110(20)	190(30)	40(20)	40(20)	-20(20)
H <sub>2</sub> O(22)	0.7063(8)	0.0064(5)	0.4930(5)	700(20)	910(60)	440(30)	740(50)	300(40)	-390(70)	-120(40)
O(23)	0.5485(6)	0.2083(3)	0.4149(3)	150(10)	180(30)	70(20)	200(30)	-50(20)	20(20)	-30(20)
H <sub>2</sub> O(24)	-0.1151(7)	0.3130(4)	-0.0376(3)	242(12)	280(30)	210(30)	240(30)	-30(20)	-30(20)	-10(20)

Table 3. Selected interatomic distances (Å) in the structure of rimkorolgitite.

Ba-O(8)a	2.673(4)	Mg(4)-O(10)e	2.023(5)	P(4)-O(23)	1.541(5)
Ba-O(3)a	2.737(5)	Mg(4)-O(16)g	2.035(5)	P(4)-O(15)	1.541(5)
Ba-O(3)	2.761(5)	Mg(4)-O(15)a	2.053(4)	P(4)-O(9)	1.545(5)
Ba-O(6)	2.855(4)	Mg(4)-O(11)	2.056(5)	P(4)-O(17)	1.554(4)
Ba-H <sub>2</sub> O(1)b	2.870(5)	Mg(4)-H <sub>2</sub> O(5)	2.127(4)	<P(4)-O>	1.55
Ba-O(6)c	2.952(5)	Mg(4)-H <sub>2</sub> O(12)h	2.436(5)	H <sub>2</sub> O(1)···O(23)	2.647(7)
Ba-O(10)	3.105(5)	<Mg(4)- $\phi$ *>	2.12	H <sub>2</sub> O(1)···H <sub>2</sub> O(12)j	2.781(7)
Ba-H <sub>2</sub> O(19)a	3.148(5)	Mg(5)-O(13)e	2.021(5)	H <sub>2</sub> O(1)···H <sub>2</sub> O(22)f	2.949(8)
Ba-O(20)c	3.212(5)	Mg(5)-O(7)	2.055(5)	H <sub>2</sub> O(1)···O(8)k	3.125(7)
Ba-O(14)	3.247(5)	Mg(5)-O(9)c	2.070(5)	H <sub>2</sub> O(2)···O(21)	2.539(7)
<Ba- $\phi$ *>	2.96	Mg(5)-O(16)i	2.065(5)	H <sub>2</sub> O(2)···O(17)l	2.620(7)
Mg(1)-O(23)f	1.987(5)	Mg(5)-H <sub>2</sub> O(2)	2.125(4)	H <sub>2</sub> O(2)···H <sub>2</sub> O(18)m	3.151(7)
Mg(1)-H <sub>2</sub> O(19)	2.004(5)	Mg(5)-H <sub>2</sub> O(12)	2.178(5)	H <sub>2</sub> O(2)···H <sub>2</sub> O(12)	3.202(6)
Mg(1)-O(13)	2.108(5)	<Mg(5)- $\phi$ *>	2.09	H <sub>2</sub> O(5)···O(21)	2.517(7)
Mg(1)-O(6)a	2.115(5)	P(1)-O(10)	1.510(5)	H <sub>2</sub> O(5)···O(17)d	2.637(7)
Mg(1)-H <sub>2</sub> O(24)	2.200(5)	P(1)-O(3)	1.513(6)	H <sub>2</sub> O(5)···H <sub>2</sub> O(18)m	3.069(7)
Mg(1)-O(3)	2.435(5)	P(1)-O(4)	1.543(4)	H <sub>2</sub> O(5)···H <sub>2</sub> O(12)a	3.152(6)
<Mg(1)- $\phi$ *>	2.14	P(1)-O(13)	1.547(5)	H <sub>2</sub> O(12)···H <sub>2</sub> O(1)n	2.781(7)
Mg(2)-O(9)c	2.039(5)	<P(1)-O>	1.53	H <sub>2</sub> O(12)···O(14)o	2.811(6)
Mg(2)-O(20)c	2.040(5)	P(2)-O(8)	1.524(5)	H <sub>2</sub> O(12)···H <sub>2</sub> O(5)p	3.152(6)
Mg(2)-O(4)	2.067(6)	P(2)-O(11)	1.527(5)	H <sub>2</sub> O(18)···H <sub>2</sub> O(24)	2.896(7)
Mg(2)-O(7)	2.071(5)	P(2)-O(7)	1.545(5)	H <sub>2</sub> O(18)···O(13)	3.051(6)
Mg(2)-H <sub>2</sub> O(5)d	2.087(4)	P(2)-O(21)	1.559(4)	H <sub>2</sub> O(18)···H <sub>2</sub> O(5)q	3.069(7)
Mg(2)-H <sub>2</sub> O(18)e	2.367(6)	<P(2)-O>	1.54	H <sub>2</sub> O(18)···O(10)	3.101(6)
<Mg(2)- $\phi$ *>	2.11	P(3)-O(14)	1.533(5)	H <sub>2</sub> O(22)···O(17)	2.788(9)
Mg(3)-O(14)a	1.989(5)	P(3)-O(16)	1.546(4)	H <sub>2</sub> O(22)···H <sub>2</sub> O(24)h	2.811(8)
Mg(3)-O(4)	2.043(6)	P(3)-O(20)	1.541(5)	H <sub>2</sub> O(22)···H <sub>2</sub> O(1)f	2.949(8)
Mg(3)-O(11)	2.083(5)	P(3)-O(6)	1.548(5)	H <sub>2</sub> O(22)···O(17)f	3.12(1)
Mg(3)-O(15)a	2.090(5)	<P(3)-O>	1.54	H <sub>2</sub> O(24)···H <sub>2</sub> O(19)	2.790(7)
Mg(3)-H <sub>2</sub> O(2)d	2.151(4)	H <sub>2</sub> O(19)···O(20)a	2.619(7)	H <sub>2</sub> O(24)···H <sub>2</sub> O(22)r	2.811(8)
Mg(3)-H <sub>2</sub> O(18)e	2.227(5)	H <sub>2</sub> O(19)···O(8)c	2.662(7)	H <sub>2</sub> O(24)···O(8)c	2.813(7)
<Mg(3)- $\phi$ *>	2.10	H <sub>2</sub> O(19)···H <sub>2</sub> O(24)	2.790(7)	H <sub>2</sub> O(24)···O(18)	2.896(7)

a =  $x-1, y, z$ ; b =  $x+1, -y-1/2, z+1/2$ ; c =  $-x, -y, -z$ ; d =  $x-1, -y-1/2, z-1/2$ ; e =  $-x, y-1/2, -z-1/2$ ; f =  $-x+1, -y, -z+1$ ; g =  $x, -y+1/2, z+1/2$ ; h =  $x+1, -y+1/2, z+1/2$ ; i =  $x, -y-1/2, z+1/2$ ; j =  $-x+1, y+1/2, -z+1/2$ ; k =  $-x, y+1/2, -z+1/2$ ; l =  $x, -y-1/2, z-1/2$ ; m =  $x, y-1, z$ ; n =  $-x+1, y-1/2, -z+1/2$ ; o =  $-x+1, -y, -z$ ; p =  $x+1, y, z$ ; q =  $x, y+1, z$ ; r =  $x-1, -y+1/2, z-1/2$   
\* $\phi$  = O, H<sub>2</sub>O

## Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. The  $R_{\text{int}}$  factors for equivalents indicated that the monoclinic symmetry is more likely and that the mineral is pseudoorthorhombic, in agreement with the suggestion of Yakubovich *et al.* (2000). Systematic absences of reflections indicated space group  $P2_1/c$ . The structure was solved by direct methods and a reasonable structure model was achieved but the  $R_1$  factor was unacceptably high (0.212). Examination of the calculated and observed structure factors revealed that the largest discrepancies corresponded to  $F_{\text{obs}}$  that were much greater than  $F_{\text{calc}}$ , a situation that is common when dealing with a merohedrally or pseudo-merohedrally twinned crystal. We incorporated twinning with the operator [100 010 00-1] using the method of Jameson (1982) and Herbst-Irmer & Sheldrick (1998), which lowered the  $R_1$  to 0.060. The final model included atomic positional and anisotropic-displacement parameters for all atoms, and a refinable weighting scheme of the structure factors. The model was refined on the basis of  $F^2$  for all 7942 unique reflec-

tions. The final refinement converged to an  $R_1$  of 0.052, calculated for the 4663 unique observed ( $|F_o| \geq 4\sigma_F$ ) reflections. We were unable to locate positions of hydrogen atoms in the structure, probably because to its twinning and presence of relatively heavy Ba atoms. Occupancy refinement for the Ba position gave a site occupancy factor (s.o.f.) of 0.949(3), whereas s.o.f. for the Mg positions are in the range of 0.92-1.04. The final atomic coordinates and anisotropic displacement parameters are in Table 2, selected interatomic distances are in Table 3, and a bond-valence analysis is provided in Table 4. A table of calculated and observed structure factors is available from the authors upon request (or through the E.J.M. Editorial Office, Paris).

## Results

### Cation polyhedra

There are five symmetrically independent Mg cations in the structure of rimkorolgitite. Each is octahedrally coordinated by four O atoms and two H<sub>2</sub>O molecules. As it can be seen

Table 4. Bond-valence analysis ( $\nu u$ ) for rimkorolgitite.

	Ba(1)	Mg(1)	Mg(2)	Mg(3)	Mg(4)	Mg(5)	P(1)	P(2)	P(3)	P(4)	$\Sigma$
H <sub>2</sub> O(1)	0.21										0.21
H <sub>2</sub> O(2)				0.29		0.31					0.60
O(3)	0.30, 0.28	0.14					1.28				2.00
O(4)			0.36	0.39			1.18				1.93
H <sub>2</sub> O(5)			0.35		0.31						0.66
O(6)	0.22, 0.17	0.32						1.16			1.87
O(7)			0.36			0.38		1.17			1.91
O(8)	0.36							1.24			1.60
O(9)			0.39			0.36				1.17	1.92
O(10)	0.11				0.41		1.29				1.81
O(11)				0.35	0.38			1.23			1.96
H <sub>2</sub> O(12)					0.13	0.27					0.40
O(13)		0.33				0.41	1.17				1.91
O(14)	0.08			0.45				1.21			1.74
O(15)				0.34	0.38				1.19		1.91
O(16)					0.40	0.37		1.17			1.94
O(17)										1.15	1.15
H <sub>2</sub> O(18)			0.16	0.24							0.40
H <sub>2</sub> O(19)	0.10	0.43									0.53
O(20)	0.08		0.39						1.19		1.66
O(21)								1.13			1.13
H <sub>2</sub> O(22)											-
O(23)		0.45								1.19	1.64
H <sub>2</sub> O(24)		0.25									0.25
$\Sigma$	1.91	1.92	2.01	2.06	2.01	2.10	4.92	4.77	4.73	4.70	

Bond-valence parameters from Brese & O'Keeffe (1991). Contributions of hydrogen bonds are not included.

from Table 3, the Mg-H<sub>2</sub>O bonds are usually longer than the Mg-O bonds. The Mg- $\phi$  bond lengths ( $\phi = \text{O}, \text{H}_2\text{O}$ ) are in the range of 1.987-2.436 Å.

One symmetrically independent Ba atom is coordinated by eight O atoms and two H<sub>2</sub>O molecules. The Ba- $\phi$  bond lengths range from 2.673 to 3.247 Å. There are four P atoms in the structure of rimkorolgitite tetrahedrally coordinated by four O atoms. The P-O bond lengths are in the range of 1.510-1.559 Å which is usual for phosphates.

### Bond-valence analysis and hydrogen bonding

The bond valence analysis presented in Table 4 was calculated using the parameters for Mg<sup>2+</sup>-O, P<sup>5+</sup>-O and Ba<sup>2+</sup>-O from Brese & O'Keeffe (1991). The bond-valence sums for all the cations are typical values for cations in similar structures. The bond-valence sums at the H<sub>2</sub>O(1), H<sub>2</sub>O(2), H<sub>2</sub>O(5), H<sub>2</sub>O(12), H<sub>2</sub>O(18), H<sub>2</sub>O(19), H<sub>2</sub>O(22) and H<sub>2</sub>O(24) sites are in the range of 0.00-0.66  $\nu u$  (valence units), in agreement with their identification as water molecules. The bond-valence sums for O sites (except O(17) and O(21) sites) are within the range of 1.60-2.00  $\nu u$ . Taking into account that contributions of hydrogen bonds are not included, these values support assignment of these sites to O atoms. The bond-valence sums for the O(17) and O(21) sites are 1.15 and 1.13  $\nu u$ . However, both these atoms have two close H<sub>2</sub>O groups each located at 2.620(7) and 2.637(7) Å for O(17), and at 2.517(7) and 2.539(7) Å for O(21). These distances clearly indicate strong hydrogen bonds that may

add at least 0.30  $\nu u$  to the bond-valence sums at anion sites each. That makes bond-valence sums at the O(17) and O(21) sites equal to at least 1.75 and 1.73  $\nu u$ , that indicate that these sites are occupied by O atoms. The same situation was observed for bakhchisaraitsevite (Yakubovich *et al.*, 2000), where authors were able to locate positions of hydrogen atoms. In bakhchisaraitsevite, the bond-valence sums for the O(5) and O(9) atoms are 1.22 and 1.25  $\nu u$ , without contributions of hydrogen bonds. If hydrogen bonds are considered, the bond-valence sums equal to 1.93 and 2.01  $\nu u$ . The crystal chemical role of the O atoms with low bond-valence sums in the structures of rimkorolgitite and bakhchisaraitsevite is quite similar – they are bonded to one P atom only. This confirms that the O(17) and O(21) sites in rimkorolgitite are occupied by O atoms. In addition, the  $U_{ij}$  values for the O(17) and O(21) atoms are comparable with those for other O atoms and do not suggest any partial protonation of these O atoms.

The anion-anion distances associated with hydrogen bonding in rimkorolgitite are given in Table 3. The H<sub>2</sub>O(1), H<sub>2</sub>O(2), H<sub>2</sub>O(5), H<sub>2</sub>O(12), H<sub>2</sub>O(22) and H<sub>2</sub>O(24) groups have two H<sub>2</sub>O...O contacts in the range of 2.52-3.13 Å and two H<sub>2</sub>O...H<sub>2</sub>O contacts in the range of 2.78-3.16 Å each. It can be suggested that the H<sub>2</sub>O groups act as hydrogen-bond donors for two O atoms and that they accept two hydrogen bonds from H<sub>2</sub>O molecules. The H<sub>2</sub>O(18) and H<sub>2</sub>O(19) groups each donate two hydrogen bonds to O atoms and accept one hydrogen bond from an H<sub>2</sub>O group.

The H<sub>2</sub>O groups in rimkorolgitite are of three types: H<sub>2</sub>O(2), H<sub>2</sub>O(5), H<sub>2</sub>O(12), H<sub>2</sub>O(18), H<sub>2</sub>O(19) and H<sub>2</sub>O(24)

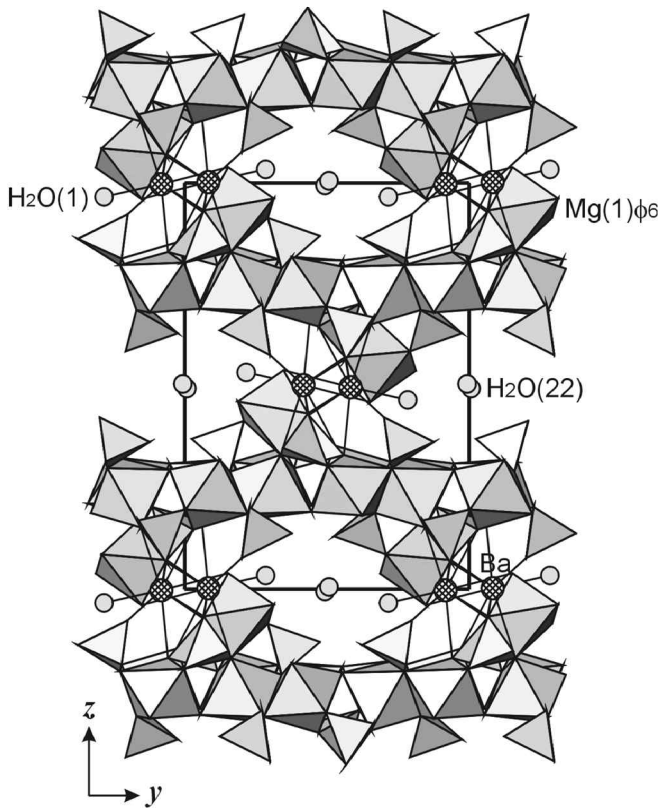


Fig. 1. Projection of the crystal structure of rimkorolgit along the  $a$  axis.

are bonded to Mg atoms only,  $\text{H}_2\text{O}(1)$  group is bonded to Ba atom, whereas  $\text{H}_2\text{O}(22)$  group forms hydrogen bonds only.

## Structure description

Fig. 1 shows a projection of the structure of rimkorolgit onto (100). The  $\text{Mg}\phi_5$  octahedra and  $\text{PO}_4$  tetrahedra form sheets parallel to (001). The Ba atoms and  $\text{H}_2\text{O}(1)$  and  $\text{H}_2\text{O}(22)$  groups are located between the sheets providing their linkage into a three-dimensional structure.

The octahedral-tetrahedral sheet consists of the  $\text{Mg}(2)\text{O}_4(\text{H}_2\text{O})_2$ ,  $\text{Mg}(3)\text{O}_4(\text{H}_2\text{O})_2$ ,  $\text{Mg}(4)\text{O}_4(\text{H}_2\text{O})_2$  and  $\text{Mg}(5)\text{O}_4(\text{H}_2\text{O})_2$  octahedra, and the  $\text{PO}_4$  tetrahedra, whereas

the  $\text{Mg}(1)\text{O}_4(\text{H}_2\text{O})_2$  octahedron is positioned above the sheet (Fig. 1). The structure of the sheet (with the exception of the  $\text{Mg}(1)\text{O}_4(\text{H}_2\text{O})_2$  octahedron) is shown in Fig. 2a. Its main element is a zigzag chain of edge-sharing octahedra. The chains are linked *via* common vertices to form an octahedral sheet in which Mg atoms are located at the vertices of the  $6^3$  hexagonal net ( $6^3$  is a Schläfli symbol for a regular honeycomb pattern that means that the net consists of hexagons and one vertex is common for three hexagons; for further references on Schläfli symbols see (Liebau, 1985; Armbruster *et al.*, 1990; O'Keeffe & Hyde, 1996)). The  $\text{PO}_4$  tetrahedra are above and below hexagonal rings of Mg octahedra and are linked to them by sharing common O vertices.

The structure of the sheet can be described in a graphical fashion using an approach recently elaborated by Hawthorne *et al.* (2000) for octahedral-tetrahedral structures in sulfate minerals. Octahedra and tetrahedra are represented by the white and black vertices, respectively. Linking of polyhedra is denoted by one, two or three edges between two vertices for corner-, edge- and face-sharing between polyhedra, respectively. The dipolyhedral sheet in rimkorolgit is graphically represented in Fig. 2b. Since moving from polyhedral to graphical representation is accompanied by lack of geometrical information (*e.g.* geometrical isomers are not distinguishable), it makes sense to describe linkage of each polyhedron by its connectivity diagram. The connectivity diagrams were proposed by Krivovichev (1997) and Krivovichev *et al.* (1997) for description of tetrahedral units with edge-sharing between tetrahedra, and recently have been adopted by Krivovichev & Burns (2000) for description of heteropolyhedral structures. For octahedral-tetrahedral structures this method can be outlined as follows: (1) as a basis for connectivity diagram, one has to use a Schlegel diagram or projection of the respective polyhedron (the latter is more convenient for octahedra); (2) heavy lines represent edges shared between the equivalent and non-equivalent polyhedra; (3) the circles indicate shared vertices, without regard to the polyhedron with which it shares an edge adjacent to the vertex; (4) the unfilled and filled circles are used to indicate that the vertex is shared with an identical or a different polyhedron, respectively. Fig. 2b shows connectivity diagrams for the polyhedra that form the sheet in the structure of rimkorolgit. As it is clearly seen, the number of polyhedra with identical connectivity diagrams (polyhedra

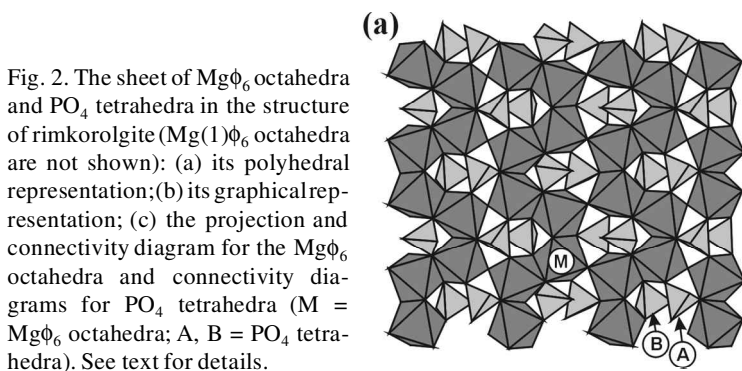


Fig. 2. The sheet of  $\text{Mg}\phi_6$  octahedra and  $\text{PO}_4$  tetrahedra in the structure of rimkorolgit ( $\text{Mg}(1)\phi_6$  octahedra are not shown): (a) its polyhedral representation; (b) its graphical representation; (c) the projection and connectivity diagram for the  $\text{Mg}\phi_6$  octahedra and connectivity diagrams for  $\text{PO}_4$  tetrahedra (M =  $\text{Mg}\phi_6$  octahedra; A, B =  $\text{PO}_4$  tetrahedra). See text for details.

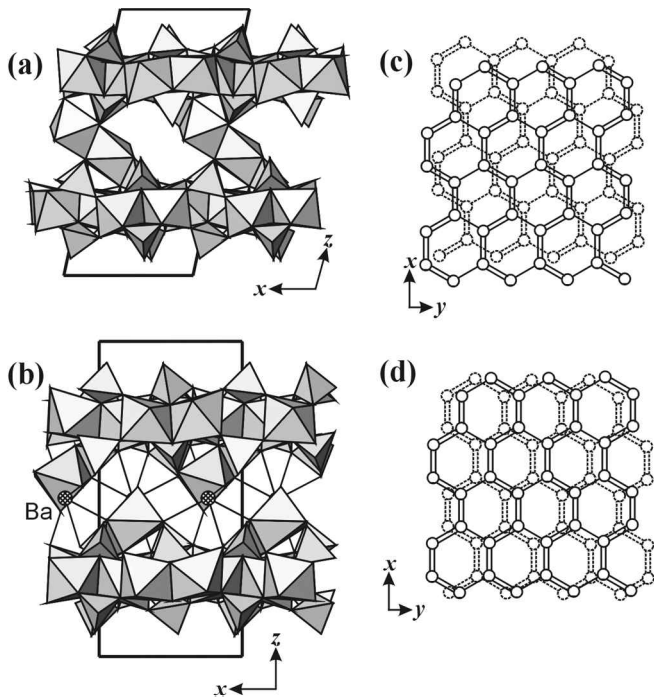


Fig. 3. Projections of the crystal structures of bakhchisaraitsevite and rimkorolgitite along the  $b$  axes (a and b, respectively) and schematic representation of the relative positions of two adjacent sheets in bakhchisaraitsevite and rimkorolgitite (c and d, respectively). Note that the octahedral-tetrahedral sheets in c and d are represented by their octahedral linkage graphs (compare with Fig. 2).

of the same topological type) is smaller than the number of crystallographically different polyhedra. The octahedra belong to one topological type, whereas there are four crystallographically non-equivalent octahedra that form the sheet shown in Fig. 2a. The tetrahedra are of two topological types, whereas they belong to four non-equivalent crystallographic types.

## Discussion

As it was suggested by Yakubovich *et al.* (2000), the structure of rimkorolgitite is closely related to that of bakhchisaraitsevite. Both structures are based on the octahedral-tetrahedral sheets of the same type that are shown in Fig. 2. However, in bakhchisaraitsevite, the sheets are linked into a three-dimensional framework by edge-sharing between the  $\text{Mg}(1)\phi_6$  octahedra from two adjacent sheets (Fig. 3a). In contrast, in rimkorolgitite, the  $\text{Mg}(1)\phi_6$  octahedra are not linked with each other but are separated by  $\text{Ba}^{2+}$  cations (Fig. 3b). Thus, the structure of rimkorolgitite can be considered as bakhchisaraitsevite-like framework interrupted by the presence of large  $\text{Ba}^{2+}$  cations.

The insertion of the  $\text{Ba}^{2+}$  cations results in a shift of the adjacent octahedral-tetrahedral sheets relative to each other. This shift is along the  $a$  axis and is accompanied by the change of  $\beta$  angle from  $102^\circ$  in bakhchisaraitsevite to  $90^\circ$  in rimkorolgitite. Figures 3c and d schematically show relative positions of the two adjacent sheets in bakhchisaraitsevite

and rimkorolgitite, respectively (the sheets are represented by graphs of octahedral linkage within them).

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