

The crystal structure of girvasite, $\text{NaCa}_2\text{Mg}_3(\text{PO}_4)_3(\text{CO}_3)(\text{H}_2\text{O})_6$, a complex phosphate carbonate hydrate based upon electroneutral heteropolyhedral layers

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Abstract

The crystal structure of girvasite, $\text{NaCa}_2\text{Mg}_3(\text{PO}_4)_3(\text{CO}_3)(\text{H}_2\text{O})_6$, has been refined using X-ray diffraction data collected at 173 K, which allowed to revise its crystal chemical formula. The mineral is monoclinic, $P2_1/c$, $a = 6.4784(2)$, $b = 12.2313(3)$, $c = 21.3494(6)$ Å, $\beta = 89.624(2)^\circ$, $V = 1691.67(8)$ Å³ (at 173 K), $Z = 4$, $R_1 = 0.037$ for 6471 unique observed reflections. The crystal structure of girvasite contains three Mg, two Ca and one Na sites. The Mg atoms are octahedrally coordinated by O atoms and H₂O molecules. The Ca sites are coordinated by eight anions each, whereas the Na site has a coordination number equal to seven. The crystal structure is based upon heteropolyhedral sheets formed by polymerization of Mg octahedra, PO₄ tetrahedra and CO₃ groups. The sheets consist of fundamental building units (FBBs) formed by two Mg octahedra that share edges to form dimers decorated by three PO₄ tetrahedra and linked to a unit consisting of a MgO₆ octahedron sharing an edge with a carbonate triangle. The FBBs polymerize to form chains running parallel to the *a* axis. The chains are further polymerized to compose heteropolyhedral sheets stuffed by the Ca²⁺ and Na⁺ cations, and H₂O groups to form electroneutral layers parallel to (001). The adjacent layers connect to each other via a complex system of hydrogen bonds. The interesting feature of the structure is a bidentate coordination of Mg²⁺ atom by a CO₃ group. The O14–Mg2–O16 angle is shortened from 90° (expected for a regular octahedron) to 60.46°, whereas the O14–C–O16 angle is shortened from 120° to 115.92°. Girvasite is the most structurally complex mineral among natural phosphate carbonates known to date. Its high structural complexity reflects its chemical complexity and high hydration state, which are the result of the specific geochemical and thermodynamic conditions of its formation (low-temperature and low-pressure interactions of phosphate-bearing solutions with primary dolomite carbonatites).

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Keywords: girvasite; crystal structure; phosphate-carbonate; complexation; structural complexity; Kola Peninsula

Introduction

Structural and chemical diversity of natural carbonates continues to attract attention of mineralogists and petrologists with several new mineral species discovered and crystal structures determined within recent few years (Lazic et al., 2011; Bindi et al., 2011; Mills et al., 2012ab; Pekov et al., 2012; McDonald et al., 2012; Miyawaki et al., 2012; Biagioni et al., 2013; Kampf et al., 2014; Elliot et al., 2014, etc.). One of the source of variable rare and exotic carbonate minerals are carbonatites that have been subject for a large number of recent detailed experimental studies (Shatskiy et al., 2013abc, 2014).

Girvasite, a rare hydrous Na-Ca-Mg phosphate carbonate, has been first described by Britvin et al. (1990) from hydrothermal veins in dolomite carbonatites of the Zhelezny (Iron) Mine, Kovdor massif, Kola Peninsula, Russia. The mineral was probably the result of reaction of primary dolomite with phosphate-bearing hydrothermal solutions. The Zhelezny mine is known as a type locality for several phosphate minerals, including rimkorolgitite, $\text{BaMg}_5(\text{PO}_4)_4(\text{H}_2\text{O})_8$ (Britvin et al., 1995; Krivovichev et al., 2002), strontio whitlockite, $\text{Sr}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$ (Britvin et al., 1991), bakhchisaraitsevite, $\text{Na}_2\text{Mg}_5(\text{PO}_4)_4(\text{H}_2\text{O})_7$ (Liferovich et al., 2000; Yakubovich et al. 2000), cattite, $\text{Mg}_3(\text{PO}_4)_2(\text{H}_2\text{O})_{22}$ (Britvin et al. 2002; Chernyatieva et al., 2013), etc.

The crystal structure of girvasite was studied by Sokolova and Yegorov-Tismenko (1990), who assigned to the mineral the crystal chemical formula $\text{NaCa}_2\text{Mg}_3(\text{OH})_2\text{H}_2(\text{PO}_4)_3(\text{CO}_3)\cdot$

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Table 1. Crystallographic data and refinement parameters for girvasite

<i>a</i> (Å)	6.4784(2)
<i>b</i> (Å)	12.2313(3)
<i>c</i> (Å)	21.3494(6)
β (°)	89.624(2)
<i>V</i> (Å ³)	1691.67(8)
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>F</i> ₀₀₀	1272
μ (cm ⁻¹)	1.211
<i>D</i> _{calc} (g/cm ⁻¹)	2.470
<i>Z</i>	4
Crystal size (mm ³)	0.07 × 0.09 × 0.12
Temperature (K)	173
Radiation MoK α	0.71073
2 θ _{max}	75.56
Total Ref.	55,166
Unique Ref.	9000
Unique F _{ol} ≤ 4 σ F	6471
<i>h</i> _{min} , <i>h</i> _{max}	−10, 11
<i>k</i> _{min} , <i>k</i> _{max}	−21, 19
<i>l</i> _{min} , <i>l</i> _{max}	−31, 36
<i>R</i> _{int}	0.0675
<i>R</i> ₁	0.0373
<i>wR</i> ₂	0.0839
<i>S</i>	1.022
ρ _{min} , ρ _{max} (e [−] Å ^{−3})	0.634, 0.748

(H₂O)₄, which assumes the simultaneous presence in the structure of both protonated tetrahedral oxyanions and hydroxyl anions. Though such a combination is known for minerals (for instance, it has recently been described by Kampf et al. (2013) for joteite, Ca₂CuAl[AsO₄][AsO₃(OH)]₂(OH)₂·5H₂O), it is very unusual and requires additional verification. Since Sokolova and Yegorov-Tismenko (1990) were unable to determine positions of H atoms in girvasite, this problem remained unresolved and awaited special consideration. In this paper, we report on the crystal-structure determination of girvasite performed at 173 K, which allowed us to identify hydrogen positions and to revise the crystal chemical formula of the mineral.

Experimental

The crystal of girvasite selected for data collection was mounted on a thin glass fiber for the X-ray diffraction analysis. More than a hemisphere of X-ray diffraction data with frame widths of 0.3° in ω , and 30 s spent counting for each frame were collected at 173 K using a Bruker four-circle Smart APEX DUO X-ray diffractometer operated at 50 kV and 40 mA with MoK α radiation. The data were integrated and corrected for absorption using an empirical ellipsoidal model

by means of the Bruker programs *APEX* and *XPREP*. The observed systematic absences were consistent with the space group *P*2₁/*c* reported for girvasite by Sokolova and Yegorov-Tismenko (1990). The structure was refined to *R*₁ = 0.052 using the atom coordinates for nonhydrogen atoms taken from Sokolova and Yegorov-Tismenko (1990). The inspection of difference Fourier electron-density map revealed the presence of twelve symmetrically independent H atoms that were incorporated into the structure refinement without any restraints. Structure refinement of the full structure model resulted in the crystallographic agreement index *R*₁ = 0.038 (Table 1). The *SHELX* program package was used for all structure calculations (Sheldrick, 2008). The final model included anisotropic displacement parameters for all nonhydrogen atoms. The final atomic coordinates and anisotropic displacement parameters are given in Table 2 and selected interatomic distances are listed in Table 3.

Results

The structure of girvasite contains three Mg, two Ca and one Na sites. The Mg atoms are octahedrally coordinated by O atoms and H₂O molecules. The Mg1 site is coordinated by five O atoms and one H₂O molecule, whereas the Mg2 and Mg3 sites are coordinated by four O atoms and two H₂O molecules each. The Ca sites are coordinated by eight anions each, whereas the Na site has a coordination number equal to seven. The local coordination environments of the Ca and Na atoms are depicted in Figs. 1a–c.

The crystal structure of girvasite can be described as based upon heteropolyhedral sheets formed by polymerization of Mg octahedra, PO₄ tetrahedra and CO₃ triangular groups. The sheets consist of fundamental building units (FBBs) shown in Fig. 2. The FBB is formed by two Mg octahedra that share edges to form dimers decorated by three PO₄ tetrahedra and linked to a unit consisting of a MgO₆ octahedron sharing an edge with a triangular carbonate group. The FBBs polymerize to form chains running parallel to the *a* axis (Fig. 3a). The chains are further polymerized to compose a heteropolyhedral sheet shown in Fig. 3b. The sheets are stuffed by the Ca²⁺ and Na⁺ cations, and H₂O groups to form electroneutral layers parallel to (001). The adjacent layers are connected to each other via a complex system of hydrogen bonds (Fig. 4).

Discussion

Carbonate groups in girvasite. The local coordination of carbonate groups in girvasite is shown in Fig. 1d. The most interesting and noteworthy feature of the structure is a bidentate (edge-sharing) coordination of Mg2 atom by a CO₃ group. As a result, both Mg₂O₆ octahedron and CO₃ group display considerable distortion. The O14–Mg2–O16 angle is shortened from 90° (expected for a regular octahedron) to 60.46°, whereas the O14–C–O16 angle is shortened from 120° to 115.92°. In order to compensate for the angle shrinkage,

Table 2. Atomic fractional coordinates and displacements parameters (\AA^2) for the crystal structure of girvasite

Atom	x	y	z	U_{eq}
Ca1	0.43801(5)	0.02010(2)	0.249925(14)	0.00498(6)
Ca2	0.67971(5)	0.25007(3)	0.348619(14)	0.00569(6)
P1	0.43834(6)	0.23332(3)	0.719833(18)	0.00503(7)
P2	0.90536(6)	0.07165(3)	0.230884(18)	0.00465(7)
P3	0.75175(6)	0.03410(3)	0.594530(18)	0.00535(7)
Mg1	0.94562(8)	0.15856(4)	0.71836(2)	0.00452(14)
Mg2	0.62007(9)	0.07221(5)	0.11156(2)	0.00610(15)
Mg3	0.25003(8)	0.02842(4)	0.63224(2)	0.00447(14)
Na	0.14773(11)	0.20757(6)	0.10527(3)	0.00967(13)
O1	0.27129(17)	0.14992(9)	0.69957(5)	0.00614(19)
O2	0.56724(18)	0.00685(9)	0.63779(5)	0.0073(2)
O3	0.91068(17)	0.00191(9)	0.75458(5)	0.0065(2)
O4	0.47074(18)	0.18180(9)	0.16814(5)	0.0073(2)
O5	0.37361(18)	0.20668(9)	0.28045(5)	0.0072(2)
O6	0.76394(18)	0.00945(9)	0.18514(5)	0.0070(2)
O7	0.97151(18)	0.17966(9)	0.20125(5)	0.0068(2)
O8	0.77604(18)	0.08853(9)	0.29220(5)	0.0064(2)
O9	0.63732(18)	0.17091(9)	0.73697(5)	0.00642(19)
O10	0.93679(17)	0.08097(9)	0.63212(5)	0.0066(2)
O11	0.17690(18)	0.07033(9)	0.43966(5)	0.0074(2)
O12	0.68505(18)	0.12025(9)	0.54579(5)	0.0073(2)
Ow13	0.02777(19)	0.19752(10)	0.81492(5)	0.0077(2)
O14	0.33790(19)	0.05346(9)	0.06098(5)	0.0076(2)
Ow15	0.79611(19)	0.17783(10)	0.05795(6)	0.0092(2)
O16	0.60557(18)	0.05677(9)	0.85916(5)	0.0071(2)
Ow17	0.2363(2)	0.05055(10)	0.94354(6)	0.0082(2)
Ow18	0.79694(19)	0.11022(10)	0.42313(5)	0.0075(2)
O19	0.82946(18)	0.10907(10)	0.93232(5)	0.0088(2)
Ow20	0.28478(19)	0.13485(10)	0.55629(6)	0.0083(2)
Ow21	0.4202(2)	0.24607(11)	0.42432(6)	0.0112(2)
C	0.7053(2)	0.03834(13)	0.91051(7)	0.0070(3)
H131	0.131(4)	0.236(2)	0.8091(12)	0.024(7)
H132	0.079(4)	0.141(2)	0.8249(12)	0.028(7)
H151	0.752(5)	0.249(2)	0.0575(14)	0.043(9)
H152	0.797(5)	0.157(2)	0.0193(14)	0.043(9)
H171	0.263(5)	0.054(2)	0.9829(14)	0.037(8)
H172	0.113(4)	0.062(2)	0.9393(12)	0.021(7)
H181	0.921(5)	0.105(2)	0.4303(14)	0.045(9)
H182	0.740(5)	0.116(3)	0.4563(16)	0.053(10)
H201	0.403(4)	0.135(2)	0.5496(11)	0.020(6)
H202	0.233(4)	0.109(2)	0.5222(12)	0.027(7)
H211	0.357(4)	0.300(2)	0.4289(11)	0.018(6)
H212	0.328(4)	0.187(2)	0.4272(11)	0.021(6)

(continued on next page)

Table 2 (continued)

Atom	U ₁₁	U ₁₂	U ₁₃	U ₂₃	U ₁₃	U ₁₂
Ca1	0.00456(12)	0.00468(13)	0.00571(12)	0.00018(9)	−0.00021(9)	−0.00038(9)
Ca2	0.00591(12)	0.00536(13)	0.00578(12)	−0.00011(10)	0.00005(9)	0.00050(10)
P1	0.00461(16)	0.00477(17)	0.00571(16)	0.00005(13)	−0.00014(12)	−0.00019(13)
P2	0.00452(16)	0.00458(17)	0.00486(16)	−0.00020(12)	−0.00021(12)	0.00004(13)
P3	0.00491(16)	0.00592(17)	0.00522(16)	−0.00029(13)	−0.00008(12)	−0.00003(13)
Mg1	0.0040(2)	0.0042(2)	0.0054(2)	−0.00011(16)	0.00015(16)	0.00011(17)
Mg2	0.0066(3)	0.0064(3)	0.0052(3)	−0.00027(18)	−0.00069(18)	0.00064(19)
Mg3	0.0043(2)	0.0045(3)	0.0046(2)	−0.00036(17)	−0.00028(16)	0.00038(17)
Na	0.0101(3)	0.0095(3)	0.0095(3)	−0.0002(2)	0.0004(2)	−0.0003(2)
O1	0.0058(5)	0.0052(5)	0.0074(5)	−0.0011(4)	−0.0002(4)	−0.0013(4)
O2	0.0062(5)	0.0096(5)	0.0063(5)	0.0006(4)	0.0012(4)	−0.0007(4)
O3	0.0049(5)	0.0059(5)	0.0086(5)	0.0006(4)	−0.0011(4)	0.0007(4)
O4	0.0069(5)	0.0065(5)	0.0086(5)	−0.0018(4)	−0.0006(4)	0.0006(4)
O5	0.0073(5)	0.0067(5)	0.0076(5)	0.0013(4)	0.0006(4)	0.0008(4)
O6	0.0078(5)	0.0066(5)	0.0067(5)	−0.0011(4)	−0.0019(4)	0.0001(4)
O7	0.0074(5)	0.0049(5)	0.0081(5)	0.0015(4)	0.0010(4)	−0.0005(4)
O8	0.0074(5)	0.0063(5)	0.0056(5)	0.0000(4)	0.0004(4)	0.0008(4)
O9	0.0059(5)	0.0060(5)	0.0073(5)	0.0005(4)	−0.0006(4)	0.0005(4)
O10	0.0051(5)	0.0079(5)	0.0070(5)	−0.0016(4)	−0.0005(4)	−0.0003(4)
O11	0.0068(5)	0.0074(5)	0.0078(5)	−0.0021(4)	−0.0004(4)	0.0007(4)
O12	0.0067(5)	0.0085(5)	0.0066(5)	0.0015(4)	−0.0012(4)	0.0007(4)
Ow13	0.0070(5)	0.0073(5)	0.0087(5)	0.0013(4)	0.0007(4)	−0.0005(4)
O14	0.0105(5)	0.0052(5)	0.0071(5)	0.0016(4)	−0.0011(4)	−0.0012(4)
Ow15	0.0124(6)	0.0074(5)	0.0080(5)	−0.0012(4)	0.0003(4)	0.0003(4)
O16	0.0077(5)	0.0069(5)	0.0068(5)	0.0003(4)	−0.0017(4)	−0.0002(4)
Ow17	0.0089(5)	0.0087(5)	0.0070(5)	−0.0005(4)	−0.0005(4)	0.0006(4)
Ow18	0.0066(5)	0.0094(5)	0.0065(5)	−0.0003(4)	0.0000(4)	0.0009(4)
O19	0.0080(5)	0.0092(5)	0.0092(5)	−0.0010(4)	−0.0020(4)	−0.0019(4)
Ow20	0.0070(5)	0.0111(5)	0.0067(5)	0.0003(4)	−0.0009(4)	−0.0008(4)
Ow21	0.0105(5)	0.0081(5)	0.0149(6)	−0.0001(4)	0.0043(4)	0.0007(4)
C	0.0071(6)	0.0073(7)	0.0066(6)	−0.0001(5)	0.0005(5)	0.0011(5)

Table 3. Selected cation–anion bond lengths (Å) and parameters of the hydrogen bond system (Å, deg) in the crystal structure of girvasite

Ca1–O3	2.2776(12)	P2–O7	1.5250(12)	Mg3–O1	2.0727(12)
Ca1–O9	2.4026(12)	P2–O3	1.5268(12)	Mg3–O2	2.0760(13)
Ca1–O5	2.4090(12)	P2–O6	1.5439(12)	Mg3–O20	2.0903(13)
Ca1–O2	2.4197(11)	P2–O8	1.5632(11)	Mg3–O18	2.0905(13)
Ca1–O8	2.5173(12)	<P2–O>	1.539	Mg3–O10	2.1287(13)
Ca1–O6	2.5199(12)	P3–O11	1.5407(12)	Mg3–O8	2.1619(12)
Ca1–O16	2.5291(12)	P3–O2	1.5423(12)	<Mg3–O>	2.102
Ca1–O4	2.6459(12)	P3–O12	1.5447(12)	NaO20	2.3632(14)
<Ca1–O>	2.465	P3–O10	1.5564(12)	NaO7	2.3639(13)
Ca2–O21	2.3251(13)	<P3–O>	1.545	NaO14	2.4392(13)

(continued on next page)

Table 3 (continued)

Ca2–O8	2.3947(11)	Mg1–O7	2.0190(13)	NaO4	2.5133(13)
Ca2–O16	2.4212(12)	Mg1–O9	2.0395(12)	NaO15	2.5243(15)
Ca2–O13	2.4478(12)	Mg1–O10	2.0725(12)	NaO1	2.7845(13)
Ca2–O18	2.4594(12)	Mg1–O3	2.0779(12)	NaO10	2.9792(13)
Ca2–O5	2.5239(12)	Mg1–O1	2.1477(12)	<Na–O>	2.567
Ca2–O9	2.5884(11)	Mg1–O13	2.1852(13)	C–O14	1.3066(19)
Ca2–O19	2.6694(12)	<Mg1–O>	2.089	C–O16	1.2958(19)
<Ca1–O>	2.478	Mg2–O6	1.9862(12)	C–O19	1.272(2)
P1O4	1.5285(12)	Mg2–O4	2.0438(12)	<C–O>	1.291
P1O5	1.5433(12)	Mg2–O15	2.0646(13)		
P1O9	1.5442(12)	Mg2–O17	2.1190(13)		
P1O1	1.5508(12)	Mg2–O14	2.1416(13)		
<P1–O>	1.541	Mg2–O16	2.2370(13)		
		<Mg2–O>	2.098		

Hydrogen bonding system

D–H	d(D–H), Å	d(H...A), Å	D–H...A	A	d(D..A), Å
Ow13–H131	0.826	1.823	164.78	O5	2.629
Ow13–H132	0.799	2.110	158.49	O6	2.869
Ow15–H151	0.913	1.680	171.47	O12	2.586
Ow15–H152	0.862	1.958	174.43	O19	2.818
Ow17–H171	0.861	1.738	174.83	O14	2.596
Ow17–H172	0.814	1.934	172.08	O19	2.743
Ow18–H181	0.824	1.721	169.67	O11	2.536
Ow18–H182	0.798	1.943	162.67	O12	2.715
Ow20–H201	0.780	1.835	170.29	O12	2.607
Ow20–H202	0.865	1.862	165.57	O11	2.708
Ow21–H211	0.784	2.010	171.13	O17	2.787
Ow21–H212	0.937	1.752	172.78	O11	2.684

Note. D, donor; A, acceptor.

Table 4. Phosphate-carbonate minerals with known crystal structures and their structural complexity parameters

Mineral name	Chemical formula	ν [atoms]	I_G [bits/at.]	$I_{G,total}$ [bits/u.c.]	Reference
Abenakiite-(Ce)	$\text{Na}_{26}\text{Ce}_6(\text{SO}_2)(\text{SiO}_3)_6(\text{PO}_4)_6(\text{CO}_3)_6$	117	4.335	507.147	(McDonald et al., 1994)
Bonshtedtite	$\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$	26	3.393	88.211	(Krivovichev et al., 2013)
Crawfordite	$\text{Na}_3\text{Sr}(\text{PO}_4)(\text{CO}_3)$	26	3.700	96.211	(Sokolova and Khomyakov, 1992)
Daqingshanite-(Ce)	$\text{Sr}_3\text{Ce}(\text{PO}_4)(\text{CO}_3)_3$	21	2.748	57.709	(Hughes and Ni, 1994)
Devitoite	$(\text{Ba}_6(\text{PO}_4)_{1.48}\text{O}_{2.08}(\text{CO}_3))(\text{Fe}_9(\text{OH})_4\text{O}_2(\text{SiO}_3)_8)$	64	5.031	322.000	(Kampf et al., 2010)
Girvasite	$\text{NaCa}_2\text{Mg}_3(\text{PO}_4)_3(\text{CO}_3)(\text{H}_2\text{O})_6$	172	5.426	933.318	(This work)
Heneuite	$\text{CaMg}_5(\text{CO}_3)(\text{PO}_4)_3(\text{OH})$	52	4.700	244.423	(Romming and Raade, 1986)
Peatite-(Y)	$\text{Li}_4\text{Na}_{12}\text{Y}_{12}(\text{PO}_4)_{12}(\text{CO}_3)_4(\text{F},\text{OH})_8$	112	4.914	550.424	(McDonald et al., 2013)
Ramikite-(Y)	$\text{Li}_4\text{Na}_{12}\text{Y}_6\text{Zr}_6(\text{PO}_4)_{12}(\text{CO}_3)_4\text{O}_4(\text{OH},\text{F})_4$	112	6.807	762.424	(McDonald et al., 2013)
Sidorenkite	$\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$	26	3.393	88.211	(Kurova et al., 1980)
Skorpionite	$\text{Ca}_3\text{Zn}_2(\text{PO}_4)_2(\text{CO}_3)(\text{OH})_2(\text{H}_2\text{O})$	50	3.844	192.193	(Krause et al., 2008)
Voggite	$\text{Na}_2\text{Zr}(\text{PO}_4)(\text{CO}_3)(\text{OH})(\text{H}_2\text{O})_2$	30	3.640	109.207	(Szymanski and Roberts, 1990)

Note. ν , Number of atoms per reduced unit cell; I_G , structural information amount per atom; $I_{G,total}$, structural information amount per unit cell.

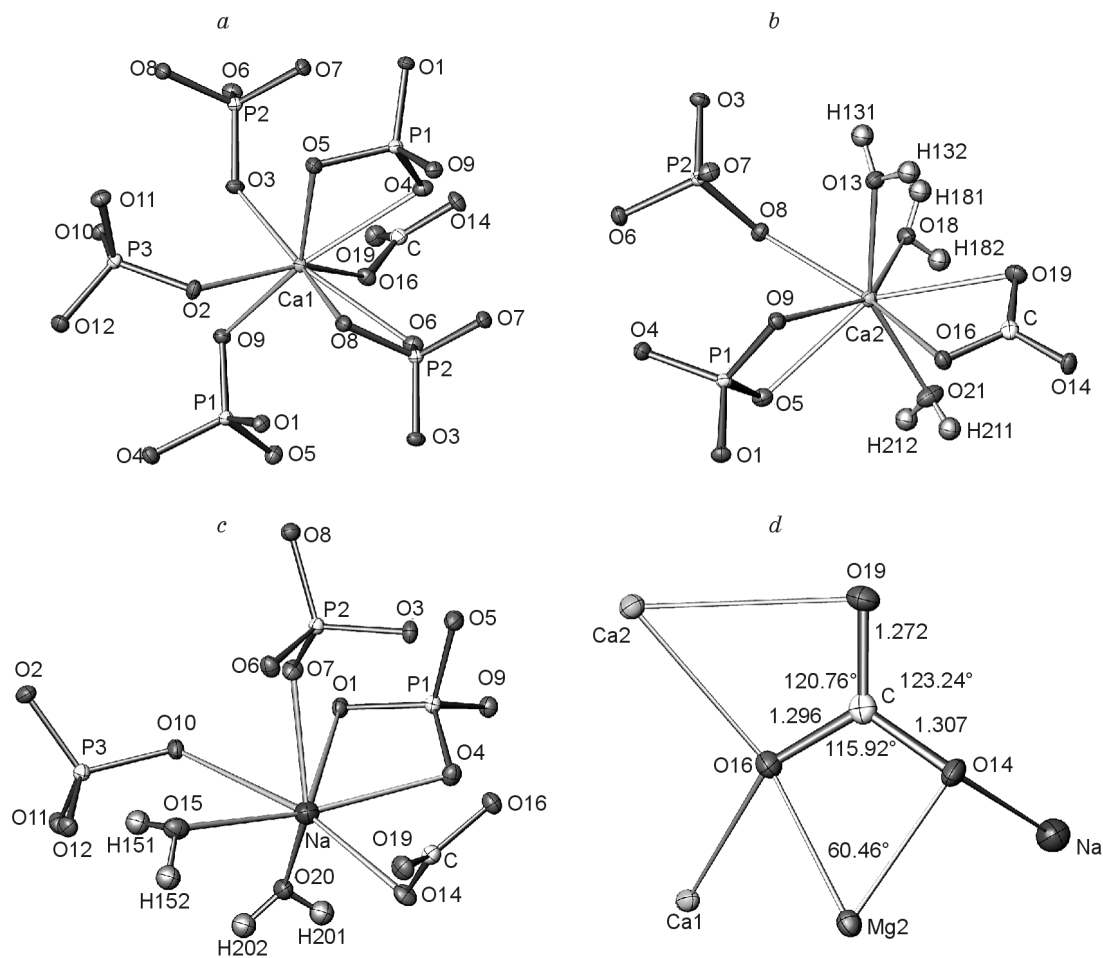


Fig. 1. Coordination environments of the Ca and Na sites (a–c) and CO₃ groups (d) in the crystal structure of girvasite (atom displacement ellipsoids are drawn at 75% probability level).

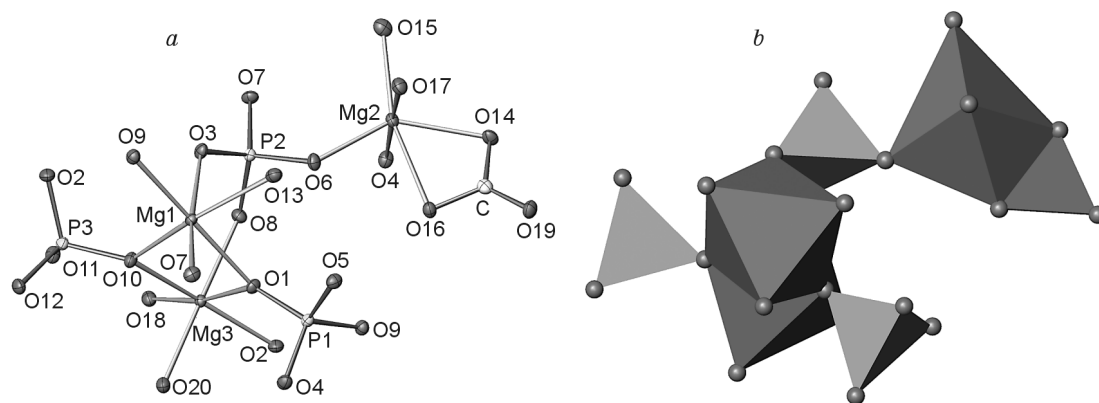


Fig. 2. Fundamental building block in the crystal structure of girvasite shown in ellipsoid (a) and polyhedral (b) representations (atom displacement ellipsoids are drawn at 75% probability level).

the C–O14 and C–O16 bonds are elongated compared to the C–O19 bond (Fig. 1d). The bidentate mode of coordination of an octahedral di- or trivalent cation by carbonate is rare in minerals, but has been observed in the crystal structures of the bradleyite-group minerals (Kurova et al., 1980; Sokolova and Khomyakov, 1992; Krivovichev et al. 2013). Bidentate

coordination is also common for natural uranyl carbonates (Krivovichev and Plášil, 2013), where UO₂²⁺ linear cations are bidentately coordinated by CO₃ groups to form stable uranyl carbonate clusters that are known to persist in aqueous solutions and to serve as transport agents of uranium in natural and technological environments (Clark et al., 1995). It may

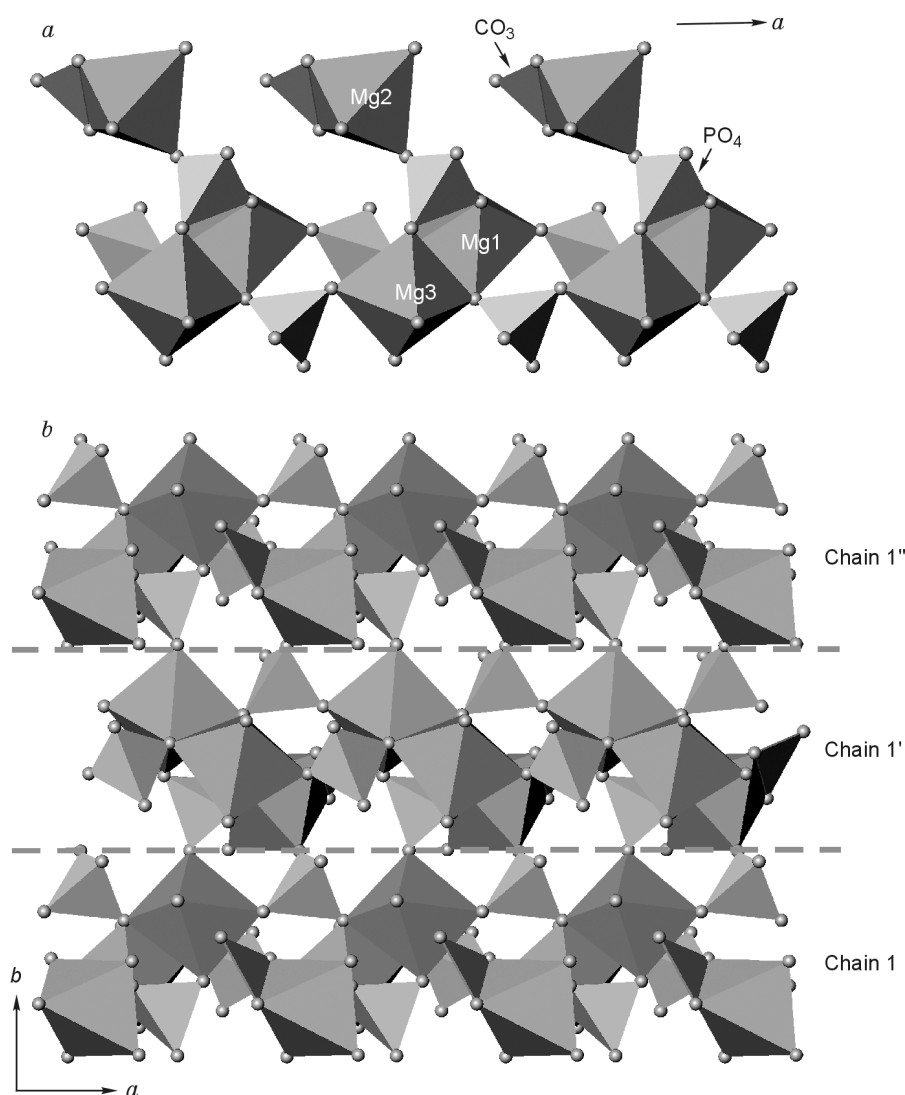


Fig. 3. One-dimensional polymerization of FBBs along the *a* axis results in the formation of complex chains (a), which are further linked along the *b* axis to form two-dimensional sheets (b) (dashed line shows the borders of the chains within the sheet).

be suggested that the bidentate complexation of Mg²⁺ cations by CO₃ groups may occur in aqueous solutions under particular conditions such as those that led to the crystallization of girvasite.

Crystal chemical formula of girvasite. As it was mentioned above, the initial formula of girvasite proposed by Sokolova and Yegorov-Tismenko (1990) on the basis of crystal-structure determination is NaCa₂Mg₃(OH)₂H₂(PO₄)₃(CO₃)(H₂O)₄. However, determination of all H sites in this work revealed no hydroxyl groups or protonated PO₄³⁻ anions. Instead, all O atoms not bonded to P⁵⁺ or C⁴⁺ cations form two strong hydrogen bonds each, thus belonging to H₂O groups. This observation allows us to revise the crystal chemical formula of girvasite as NaCa₂Mg₃(PO₄)₃(CO₃)(H₂O)₆. This formula excludes simultaneous occurrence of the basic (OH)⁻ and acid (PO₃OH)²⁻ anions originally postulated for girvasite by Sokolova and Yegorov-Tismenko (1990).

Structural complexity of girvasite and related minerals. The complexity of the atomic arrangement in girvasite can be

quantitatively evaluated as an information amount in bits per unit cell ($I_{G,total}$) using the formula (Krivovichev, 2013, 2014):

$$I_{G,total} = -v I_G = -v \sum_{i=1}^k p_i \log_2 p_i \text{ (bits/u.c.)},$$

where k is the number of different crystallographic orbits, I_G is the information amount per atom, and p_i is the random choice probability for an atom from the i th crystallographic orbit, that is:

$$p_i = m_i / v,$$

where m_i is a multiplicity of a crystallographic orbit relative to the reduced unit cell, and v is the number of atoms in the reduced unit cell.

The $I_{G,total}$ value for girvasite is 933.318 bits per unit cell, which places it among the class of complex minerals (500–1000 bits/u.c.). This relatively high level of complexity of the crystal structure of girvasite is comparable to that observed

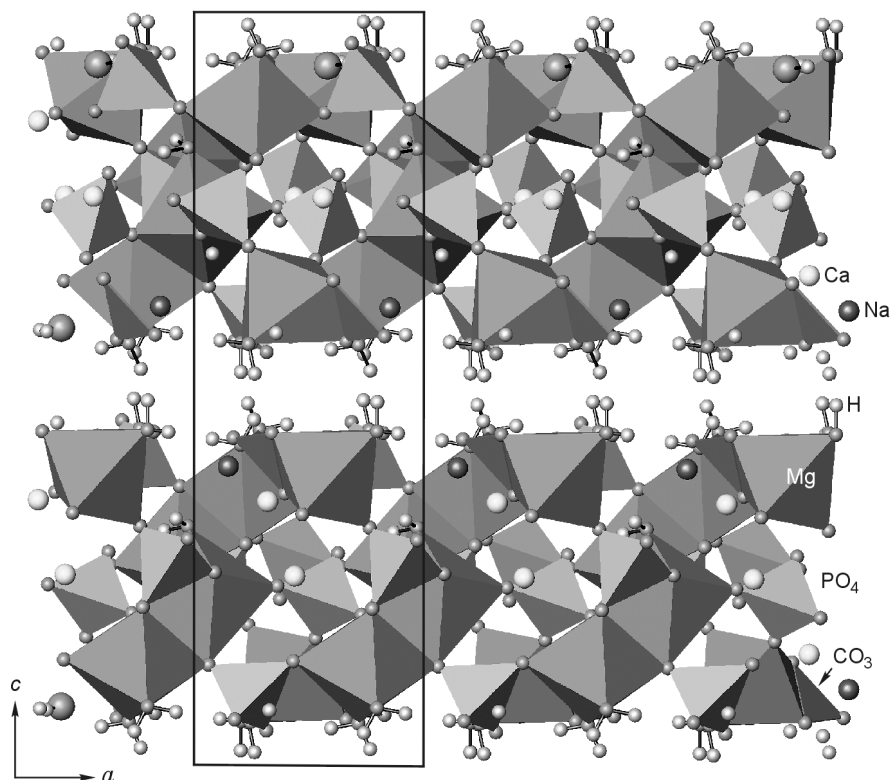


Fig. 4. The crystal structure of girvasite projected parallel to the *b* axis.

for other rare Mg-bearing phosphate minerals first described from the Zhelezny mine of the Kovdor massif: rimkoroligite, $\text{BaMg}_5(\text{PO}_4)_4(\text{H}_2\text{O})_8$ (691.895 bits/u.c.), bakhchisaraitsevite, $\text{Na}_2\text{Mg}_5(\text{PO}_4)_4(\text{H}_2\text{O})_7$ (1128.771 bits/u.c.), cattiiite, $\text{Mg}_3(\text{PO}_4)_2(\text{H}_2\text{O})_{22}$ (419.999 bits/u.c.), and strontio whitlockite, $\text{Sr}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$ (375.031 bits/u.c.). The high structural complexity of the minerals clearly reflects their chemical complexity and high hydration states (except for strontio whitlockite), which are the results of the specific geochemical and thermodynamic conditions (low-temperature and low-pressure interactions of phosphate-bearing solutions with primary dolomite carbonatites). It is of interest that girvasite is the most structurally complex mineral among natural phosphate carbonates known to date (see Table 4 for a list of phosphate-carbonate minerals and their structural complexity parameters).

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References

- Biagioni, C., Bonaccorsi, E., Camara, F., Cadoni, M., Ciriotti, M.E., Bersani, D., Kolitsch, U., 2013. Lusernaite-(Y), $\text{Y}_4\text{Al}(\text{CO}_3)_2(\text{OH},\text{F})_{11}\cdot 6\text{H}_2\text{O}$; a new mineral species from Luserna Valley, Piedmont, Italy; description and crystal structure. *Am. Mineral.* 98, 1322–1329.
- Bindi, L., Nestola, F., Kolitsch, U., Guastoni, A., Zorzi, F., 2011. Fassinaite, $\text{Pb}_2^{2+}(\text{S}_2\text{O}_3)(\text{CO}_3)$, the first mineral with coexisting thiosulphate and carbonate groups: description and crystal structure. *Mineral. Mag.* 75, 2721–2732.
- Britvin, S.N., Pakhomovskii, Y.A., Bogdanova, A.N., Sokolova, E.V., 1990. Girvasite, a new carbonate-phosphate of sodium, calcium and magnesium. *Mineralogicheskii Zh.* 12, 79–83.
- Britvin, S.N., Pakhomovskii, Y.A., Bogdanova, A.N., Skiba, V.I., 1991. Strontio whitlockite, $\text{Sr}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$, a new mineral species from the Kovdor deposit, Kola-Peninsula, USSR. *Can. Mineral.* 29, 87–93.
- Britvin, S.N., Pakhomovskii, Y.A., Bogdanova, A.N., Khomyakov, A.P., Krasnova, N.I., 1995. Rimkoroligite, $(\text{Mg},\text{Mn})_5(\text{Ba},\text{Sr},\text{Ca})(\text{PO}_4)_4\cdot 8\text{H}_2\text{O}$, a new mineral. *Zap. Vses. Mineral. Obshch.* 124, 90–95.
- Britvin, S.N., Ferraris, G., Ivaldi, G., Bogdanova, A.N., Chukanov, N.V., 2002. Cattiiite, $\text{Mg}_3(\text{PO}_4)_2\cdot 22\text{H}_2\text{O}$, a new mineral from Zhelezny mine (Kovdor Massif, Kola Peninsula, Russia). *N. Jb. Mineral. Mh.* 2002, 160–168.
- Chernyatieva, A.P., Krivovichev, S.V., Britvin, S.N., 2013. The crystal structure of cattiiite, $\text{Mg}_3(\text{PO}_4)_2(\text{H}_2\text{O})_{22}$. *Zap. Ross. Mineral. Obshch.* 142 (2), 120–128 [Geol. Ore Deposits, 2014, in press].
- Clark, D.L., Hobart, D.E., Neu, M.P., 1995. Actinide carbonate complexes and their importance in actinide environmental chemistry. *Chem. Rev.* 95, 25–48.
- Elliott, P., Giester, G., Rowe, R., Pring, A., 2014. Putnisite, $\text{SrCaCr}_8^{3+}(\text{CO}_3)_8\text{SO}_4(\text{OH})_{16}\cdot 25\text{H}_2\text{O}$, a new mineral from Western Australia: description and crystal structure. *Mineral. Mag.* 78, 131–144.
- Hughes, J.M., Ni, Y., 1994. A high-precision crystal structure refinement of daqingshanite-(Ce) from Nkombwa Hill carbonatite, Zambia. *Mineral. Mag.* 58, 493–496.
- Kampf, A.R., Rossman, G.R., Steele, I.M., Pluth, J.J., Dunning, G.E., Walstrom, R.E., 2010. Devitoite, a new heterophyllosilicate mineral with astrophyllite-like layers from Eastern Fresno County, California. *Can. Mineral.* 48, 29–40.

- Kampf, A.R., Mills, S.J., Housley, R.M., Rossman, G.R., Nash, B.P., Dini, M., Jenkins, R.A., 2013. Joteite, $\text{Ca}_2\text{CuAl}[\text{AsO}_4][\text{AsO}_3(\text{OH})]_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, a new arsenate with a sheet structure and unconnected acid arsenate groups. *Mineral. Mag.* 77, 2811–2823.
- Kampf, A.R., Mills, S.J., Housley, R.M., Marty, J., 2014. Lead-tellurium oxysalts from Otto Mountain near Baker, California: IX. Agaite, $\text{Pb}_3\text{Cu}^{2+} \cdot \text{Te}^{6+}\text{O}_5(\text{OH})_2(\text{CO}_3)$, a new mineral with CuO_5 – TeO_6 polyhedral sheets. *Am. Mineral.* 98, 512–517.
- Krause, W., Effenberger, H., Bernhardt, H.J., Medenbach, O., 2008. Skorpionite, $\text{Ca}_3\text{Zn}_2(\text{PO}_4)_2(\text{CO}_3)(\text{OH})_2(\text{H}_2\text{O})$, a new mineral from Namibia: description and crystal structure. *Eur. J. Mineral.* 20, 271–280.
- Krivovichev, S.V., 2013. Structural complexity of minerals: information storage and processing in the mineral world. *Mineral. Mag.* 77, 275–326.
- Krivovichev, S.V., 2014. Which inorganic structures are the most complex? *Angew. Chem. Int. Ed.* 53, 654–661.
- Krivovichev, S.V., Plášil, J., 2013. Mineralogy and crystallography of uranium, in: Burns, P.C., Sigmon, G.E. (Eds), *Uranium: Cradle to Grave*. Mineralogical Association of Canada Short Course Ser. Vol. 43, pp. 15–120.
- Krivovichev, S.V., Britvin, S.N., Burns, P.C., Yakovenchuk, V.N., 2002. Crystal structure of rimkorolite, $\text{Ba}[\text{Mg}_5(\text{H}_2\text{O})_7(\text{PO}_4)_4](\text{H}_2\text{O})$, and its comparison with bakhchisaraitsevite. *Eur. J. Mineral.* 14, 397–402.
- Krivovichev, S.V., Chernyatjeva, A.P., Britvin, S.N., Yakovenchuk, V.N., Krivovichev, V.G., 2013. Refinement of the crystal structure of bonstedtite, $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$. *Geol. Ore Deposits* 55, 669–675.
- Kurova, T.A., Shumyatskaya, N.G., Voronkov, A.A., Pyatenko, Yu.A. (1980) Crystal structure of sidorenkite $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$. *Dokl. Akad. Nauk SSSR* 251, 605–607.
- Lazic, B., Armbruster, T., Savelyeva, V.B., Zadov, A.E., Pertsev, N.N., and Dzierzanowski, P., 2011. Galuskinite, $\text{Ca}_7(\text{SiO}_4)_3(\text{CO}_3)$, a new skarn mineral from the Birkhin gabbro massif, Eastern Siberia, Russia. *Mineral. Mag.* 75, 2631–2648.
- Liferovich, R.P., Pakhomovsky, Ya.A., Yakubovich, O.V., Massa, W., Laajoki, K., Gehör, S., Bogdanova, A.N., Sorokhtina, N.V., 2000. Bakhchisaraitsevite, $\text{Na}_2\text{Mg}_5[\text{PO}_4]_4 \cdot 7\text{H}_2\text{O}$, a new mineral from hydrothermal assemblages related to phoscorite–carbonatite complex of the Kovdor massif, Russia. *N. Jb. Miner. Mh.* 2000, 402–418.
- McDonald, A.M., Chao, G.-Y., Grice, J.D., 1994. Abenakiite-(Ce), a new silicophosphate carbonate mineral from Mont Saint-Hilaire, Quebec: description and structure determination. *Can. Mineral.* 32, 843–854.
- McDonald, A.M., Back, M.E., Gault, R.A., Horváth, L., 2013. Peatite-(Y) and ramikite-(Y), two new Na–Li–Y \pm Zr phosphate-carbonate minerals from the Poudrette pegmatite, Mont Saint-Hilaire, Quebec. *Can. Mineral.* 51, 569–596.
- Mills, S.J., Christy, A.G., Genin, J.-M.R., Kameda, T., Colombo, F., 2012a. Nomenclature of the hydrotalcite supergroup: natural layered double hydroxides. *Mineral. Mag.* 76, 1289–1336.
- Mills, S.J., Kartashov, P.M., Kampf, A.R., Konev, A.A., Koneva, A.A., Raudsepp, M., 2012b. Cordylite-(La), a new mineral species in fenite from the Biraya Fe–REE deposit, Irkutsk, Russia. *Can. Mineral.* 50, 1281–1290.
- Miyawaki, R., Yokoyama, K. and Husdal, T.A., 2013. Bastnäsite-(Nd), a new Nd-dominant member of the bastnäsite group from the Stetind pegmatite, Tysfjord, Nordland, Norway. *Eur. J. Miner.* 25, 187–191.
- Pekov, I.V., Chukanov, N.V., Britvin, S.N., Kabalov, Yu.K., Göttlicher, J., Yapaskurt, V.O., Zadov, A.E., Krivovichev, S.V., Schüller, W., Terneš, B., 2012. The sulfite anion in ettringite-group minerals: a new mineral species hielscherite, $\text{Ca}_3\text{Si}(\text{OH})_6(\text{SO}_4)(\text{SO}_3) \cdot 11\text{H}_2\text{O}$, and the thaumasite–hielscherite solid-solution series. *Mineral. Mag.* 76, 1133–1152.
- Romming, C., Raade, G., 1986. The crystal structure of heneuite, $\text{CaMg}_5(\text{CO}_3)(\text{PO}_4)_3(\text{OH})$. *N. Jb. Miner. Mh.* 1986, 351–359.
- Shatskiy, A., Sharygin, I.S., Litasov, K.D., Borzdov, Y.M., Palyanov, Y.N., Ohtani, E., 2013a. New experimental data on phase relations for the system Na_2CO_3 – CaCO_3 at 6 GPa and 900–1400 °C. *Am. Mineral.* 98, 2164–2171.
- Shatskiy, A., Gavryushkin, P.N., Sharygin, I.S., Litasov, K.D., Kupriyanov, I.N., Higo, Y., Borzdov, Yu.M., Funakoshi, K., Palyanov, Yu.N., Ohtani, E., 2013b. Melting and subsolidus phase relations in the system Na_2CO_3 – MgCO_3 – H_2O at 6 GPa and the stability of $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ in the upper mantle. *Am. Mineral.* 98, 2172–2182.
- Shatskiy, A., Sharygin, I.S., Gavryushkin, P.N., Litasov, K.D., Borzdov, Yu.M., Shcherbakova, A.V., Higo, Y., Funakoshi, K., Palyanov, Yu.N., Ohtani, E., 2013c. The system K_2CO_3 – MgCO_3 at 6 GPa and 900–1450 °C. *Am. Mineral.* 98, 1593–1603.
- Shatskiy, A., Borzdov, Yu.M., Litasov, K.D., Kupriyanov, I.N., Ohtani, E., Palyanov, Yu.N., 2014. Phase relations in the system FeCO_3 – CaCO_3 at 6 GPa and 900–1700 °C and its relation to the system CaCO_3 – FeCO_3 – MgCO_3 . *Am. Mineral.* 99, 773–785.
- Sheldrick, G.M., 2008. A short history of SHELX. *Acta Crystallogr.* A64, 112–122.
- Sokolova, E.V., Khomyakov, A.P., 1992. Crystal structure of a new mineral $\text{Na}_3\text{SrPO}_4\text{CO}_3$ from bredleyite group. *Dokl. Akad. Nauk SSSR* 322, 531–535.
- Sokolova, E.V., Yegorov-Tismenko, Y.K., 1990. Crystal structure of girvasite. *Dokl. AN SSSR* 331, 1372–1376 (in Russian).
- Szymanski, J.T., Roberts, A.C., 1990. The crystal structure of voggite, a new hydrated Na–Zr hydroxide-phosphate-carbonate mineral. *Mineral. Mag.* 54, 495–500.
- Yakubovich, O.V., Massa, W., Liferoich, R.P., Pakhomovsky, Y.A., 2000. The crystal structure of bakhchisaraitsevite, $[\text{Na}_2(\text{H}_2\text{O})_2]\{(\text{Mg}_{4.5}\text{Fe}_{0.5})(\text{PO}_4)_4(\text{H}_2\text{O})_5\}$, a new mineral species of hydrothermal origin from the Kovdor phoscorite–carbonatite complex, Russia. *Can. Mineral.* 38, 831–838.