= NEW MINERALS =====

Günterblassite, $(K,Ca)_{3-x}$ Fe[$(Si,Al)_{13}O_{25}(OH,O)_4$] · 7H₂O, a New Mineral: the First Phyllosilicate with Triple Tetrahedral Layer¹

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Received September 22, 2011

Abstract—A new mineral, günterblassite, has been found in the basaltic quarry at Mount Rother Kopf near Gerolstein, Rheinland—Pfalz, Germany as a constituent of the late assemblage of nepheline, leucite, augite, phlogopite, åkermanite, magnetite, perovskite, a lamprophyllite-group mineral, götzenite, chabazite-K, chabazite-Ca, phillipsite-K, and calcite. Günterblassite occurs as colorless lamellar crystals up to $0.2 \times 1 \times 1.5$ mm in size and their clusters. The mineral is brittle, with perfect cleavage parallel to (001) and less perfect cleavage parallel to (100) and (010). The Mohs hardness is 4. The calculated and measured density is 2.17 and 2.18(1) g/cm³, respectively. The IR spectrum is given. The new mineral is optically biaxial and positive as follows: $\alpha = 1.488(2)$, $\beta = 1.490(2)$, $\gamma = 1.493(2)$, $2V_{meas} = 80(5)^{\circ}$. The chemical composition (electron microprobe, average of seven point analyses, H₂O is determined by gas chromatography, wt %) is as follows: 0.40 Na₂O, 5.18 K₂O, 0.58 MgO, 3.58 CaO, 4.08 BaO, 3.06 FeO, 13.98 Al₂O₃, 52.94 SiO₂, 15.2 H₂O, and

the total is 98.99. The empirical formula is Na_{0.15}K_{1.24}Ba_{0.30}Ca_{0.72}Mg_{0.16}F $e_{0.48}^{2+}$ [Si_{9.91}Al_{3.09}O_{25.25}(OH)_{3.75}] · 7.29H₂O. The crystal structure has been determined from a single crystal, R = 0.049. Günterblassite is orthorhombic, space group *Pnm2*₁; the unit-cell dimensions are a = 6.528(1), b = 6.970(1), c = 37.216(5) Å, V = 1693.3(4) Å³, Z = 2. Günterblassite is a member of a new structural type; its structure is based on three-layer block [Si₁₃O₂₅(OH,O)₄]. The strong reflections in the X-ray powder diffraction pattern [d Å (I, %) are as follows: 6.532(100), 6.263(67), 3.244(49), 3.062(91), 2.996(66), 2.955(63), and 2.763(60). The mineral was named in honor of Günter Blass (born in 1943), a well-known amateur mineralogist and specialist in electron microprobe and X-ray diffraction. The type specimen of günterblassite is deposited in the collections of the Fersman Mineral-ogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 4107/1. **DOI:** 10.1134/S1075701512080065

INTRODUCTION

The topological diversity of tetrahedral layers, primarily composed of silicate and aluminosilicate tetrahedra, is great in the structures of minerals (*Mineraly*, 1992) and permanently increases. In particular, the crystal structures of three hydrous calc-alkaline silicates comprising the mountainite family were solved recently: proper mountainite $KNa_2Ca_2[Si_8O_{19}(OH)] \cdot$ $6H_2O$ (Zubkova et al., 2009) and related new minerals shlykovite $KCa[Si_4O_9(OH)] \cdot 3H_2O$ and cryptophyllite $K_2Ca[Si_4O_{10}] \cdot 5H_2O$ (Pekov et al., 2010; Zubkova et al., 2010). In these minerals, the eight- and four-tetrahedra rings that are similar to those in apophyllite, but differ in their orientation of tetrahedra can be distinguished within the $[Si_8Ø_{20}]$ layer (where $\emptyset = O$, OH). The individual feature of the mountainite-family minerals is the position of the pendant (not shared with other tetrahedra) apex of one of Si-tetrahedra in the four-member ring opposite to the direction of other three apices relative to the plane of the layer. In shlykovite and cryptophyllite, all four-membered rings in the layer have the same orientation (the shlykovite-type layer), whereas in mountainite, the layer consists of alternating chains of such rings rotated 180° relative to each other (Zubkova et al., 2010).

¹ The new mineral species günterblassite and its name were approved by the Commission on New Minerals, Nomenclature, and Mineral Classification of the International Mineralogical Association on June 2, 2011 (IMA no. 2011-032).

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Fig. 1. Crystals of günterblassite. Width of image is 3 mm. Photo by V. Betz.

Two shlykovite layers shared by apices of tetrahedra form a specific double layer, known as a two-layer tetrahedral packet, or module $[Si_8 Ø_{19}]$, where Ø = O, OH. This layer is known from the structures of rhodesite $K_{1-x}Na_{x+2y}Ca_{2-y}[Si_8O_{18}(OH)] \cdot (6-z)H_2O$, macdonaldite BaCa₄[Si₈O₁₈(OH)]₂ \cdot 10H₂O, seidite-(Ce) $Na_4(Ce,Sr)_2Ti[Si_8O_{18}(OH)](O,OH,F)_5 \cdot 5H_2O$, and monteregianite-(Y) KNa₂Y[Si₈O₁₉] · 5H₂O. Similar but aluminosilicate double layers occur in delhavelite $K_4Na_2Ca_2[Si_7AlO_{19}]F_2Cl$, fivegite $K_4Ca_2[Si_7AlO_{17}(O_{2-x}OH_x]Cl, and hydrodelhayelite$ $KCa_2[Si_7AlO_{17}(OH)_2](H_2O)_{6-x}$ (Ferraris and Gula, 2005; Pekov et al., 2009, 2011a). All these minerals and related synthetic compounds are combined into the rhodesite mero-plesiotype series, in which the aluminosilicate branch, i.e., the delhayelite family, is distinguished (Cadoni and Ferraris, 2009; Pekov et al., 2011b).

The new mineral species described in this article is the first phyllosilicate with a triple tetrahedral layer (triple-layer tetrahedral packet, or module). The mineral was named günterblassite in honor of Günter Blass (born in 1943), a well-known amateur mineralogist and specialist in electron microprobe and X-ray diffraction analyses who has carried out many analyses of minerals (predominantly from the Eifel region) and is the coauthor of descriptions of several new mineral species, including pattersonite, allanpringite, schäferite, lukrahnite, hechtsbergite, ferriallanite-(La), windhoekite, and perrierite-(La).

The type specimen of günterblassite is deposited in the collections of the Fersman Mineralogical Museum

of the Russian Academy of Sciences, Moscow, Russia with the registration number 4107/1.

OCCURRENCE

The specimens with günterblassite were collected in 2010 in the operating basaltic quarry at Mount Rother Kopf, Roth community, near Gerolstein, Rheinland—Pfalz, Germany. The new mineral was discovered as a member of the late mineral assemblage that consists of nepheline, leucite, augite, phlogopite, akermanite, magnetite, perovskite, barium minerals of the lamprophyllite group, götzenite, and fluorapatite, after which the low-temperature chabazite-K, chabazite-Ca, phillipsite-Ca, and calcite crystallized. The crystals of all these minerals encrust the walls of miaroles in alkali basalt.

MORPHOLOGY AND PHYSICAL PROPERTIES

Günterblassite occurs as flattened from thin lamellar to tabular crystals up to $0.2 \times 1 \times 1.5$ mm in size (Fig. 1) and their near-parallel or sheaf-shaped aggregates up to 3 mm across. Simply faced crystals, such as rectangular lamellae or plates formed only by the faces of three pinacoids, are the most typical, i.e., {001} (major habit form), {010} and {100} (side faces). These crystals are supplemented by less common faces of rhombic prism {110} and the {*h0l*} and/or {0*kl*} face belts, which are uneven and convex and, thus, difficult to measure and index. The epitactic or more frequent syntactic intergrowth of the new mineral with nepheline and the lamprophyllite-group members are common (Fig. 2). The {001} faces of günterbalssite are



Fig. 2. Intergrowth of günterblassite with a lamprophyllite-group mineral. Width of image is 3 mm. Photo by V. Betz.



Fig. 3, IR spectrum of günterblassite.

parallel (coplanar) to $\{100\}$ faces and occasionally $\{001\}$ of nepheline and $\{001\}$ of the lamprophyllitetype minerals. Irregular intergrowths of the new mineral and nepheline or leucite are observed frequently.

Günterblassite is usually colorless and water-transparent; occasionally, its crystals are white, pale yellow, or brown; the streak is white. The mineral is brittle with Mohs hardness 4; the perfect cleavage is parallel to (001) and less perfect, to (100) and (010). The calculated density is 2.17 g/cm^3 , while the density measured by equilibration in heavy liquids is $2.18(1) \text{ g/cm}^3$.

Wide bands in the IR spectrum of günterblassite (Fig. 3) reflect cation disordering in the structure (see below). Absorption bands and their assignments are as follows (given in cm⁻¹; s is strong band and sh is shoulder): 3610sh, 3400s, 3230sh (O–H stretching vibrations); 1650 (bending vibrations of H₂O molecules); 1175sh, 1037s, 900sh (Si–O stretching vibrations); 780sh, 704, 630sh, 596 (O–Si–O bending vibrations); and 442s, 380sh (combination of Si–O–Si bending

vibrations and stretching vibrations of the MO_7 polyhedra, where $M = \text{Fe}^{2+}$, Ca, Mg).

Bands of B- and C-bearing groups between 1200 and 1500 cm^{-1} are not detected in the IR spectrum of günterblassite.

The new mineral is optically biaxial, positive: $\alpha = 1.488(2)$, $\beta = 1.490(2)$, $\gamma = 1.493(2)$, $2V_{\text{meas}} = 80(5)^{\circ}$, $2V_{\text{calc}} = 79^{\circ}$. No dispersion of the optical axes is observed. The optical orientation is Z = c; axes of optical indicatrix are perpendicular to cleavage planes.

CHEMICAL COMPOSITION

The chemical composition of günterblassite was determined on a Tescan Vega II XMU SEM equipped with an INCAx-sight EDS that operate on a tungsten cathode at an accelerating voltage of 15.7 kV. The current of the absorbed electrons on Co was 0.5 nA. The angle of selection of X-ray radiation was 35° and the focal distance between the sample and detector was 25 mm.

The H_2O content was measured via gas chromatography of the annealing products at 1400°C with a vario MICRO cube instrument.

The measured chemical composition (wt %) is given in Table 1. The empirical formula of günterblassite calculated based on $(Si,Al)_{13}(O,OH)_{29}$ (according to the structural data) is $Na_{0.15}K_{1.24}Ba_{0.30}Ca_{0.72}Mg_{0.16}Fe_{0.48}^{2+}$ [Si_{9.91}Al_{3.09} $O_{25,25}(OH)_{3.75}$] \cdot 7.29H₂O. The idealized formula is

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

 $(K,Ca)_{3}Fe[(Si,Al)_{13}O_{25}(OH,O)_{4}] \cdot 7H_{2}O.$

The X-ray powder diffraction pattern of günterbalssite (Table 2) was recorded on a Stoe IPDS II single-crystal diffractometer with an image plate detector, MoKa radiation, an accelerating voltage of 45 kV, and a current of 30 mA. The measurements were carried out using the Gandolfi method by rotation around two axes (ω and φ); the distance between the sample and detector was 200 mm and the measurement time was 60 min.

All reflections of the X-ray powder diffraction pattern of günterblasite are readily indexed in the orthorhombic unit cell with the following unit-cell dimensions refined by the least squares method: a = 6.522(8), b = 6.972(8), c = 37.21(4) Å, and V = 1692(6) Å³.

The X-ray single-crystal data were collected with an Xcalibur CCD diffractometer and MoK α radiation. The orthorhombic (space group *Pnm*2₁) unit-cell dimensions from these data are as follows: a =6.528(1), b = 6.970(1), c = 37.216(5) Å, V = 1693.3(4)Å³, and Z = 2.

The crystal structure of the new mineral was solved using 2706 unique reflections with $|F| > 3\sigma(F)$, R = 0.049. Detailed structural data on günterblassite have been reported by Rastsvetaeva et al. (2012); only a brief characterization is given below.

The structure of the new mineral is based on a triple-layered packet (module) $[T_{13}O_{25}(OH,O)_4]$, where

Table 1. Chemical composition of günterblassite (averageof seven microprobe point analyses)

Component	Content, wt %	Range of contents	Standard
Na ₂ O	0.40	0.14-0.67	Albite
K ₂ O	5.18	4.28-5.91	Microcline
MgO	0.58	0.42-0.81	Diopside
CaO	3.58	2.99-3.89	Wollastonite
BaO	4.07	3.55-5.08	BaF ₂
FeO	3.06	2.43-3.85	Fe ₂ O ₃
Al_2O_3	13.98	13.60-14.26	Al_2O_3
SiO ₂	52.94	52.20-54.23	SiO ₂
H ₂ O	15.2		
Total	98.99		

Note: F, P, S, Cl, Ti, Cr, Mn, and Sr contents are below detection limits.

T = Si, Al (Fig. 4). The module consists of three SiO layers that are shared by apices of Si-tetrahedra and pierced by zeolite channels in the [010] and [100] directions. Si and Al atoms are disordered in the packet. The outer shlykovite-type layers $[T_{24}O_9(O,OH)]$ differ from the inner $[T_5O_{11}]$ layer in an additional tetrahedron SiO₄.

Unlike the minerals of the mountainite and delhayelite families, where the columns of completely occupied edge-shared Ca-centred octahedra are pressed between the tetrahedral layers (packets) (Cadoni and Ferraris, 2009; Pekov et al., 2011b), in the structure of günterblassite, cations of moderate force strengths (Fe, Mg, Ca) form isolated septatopes (Fe,Ca,Mg)[O₂(OH)₂(H₂O)₃] (with the cation–anion distance ranging from 2.380 to 2.726 Å), which sew tetrahedral packets together to form an original heteropolyhedral framework (Fig. 5). K, Ba, Na, and partially Ca ions and coordinating H₂O molecules reside in interlayer and fill channels in the triple-layered packet. The extra framework sites are partially vacant.



Fig. 4. Triple tetrahedral packet of günterblassite.

I _{meas} ,%	d _{meas} , Å	$I_{\rm calc},\%$	$d_{ m calc}, { m \AA}^*$	hkl
13	9.30	15	9.304	004
45	6.885	46	6.851	011
100	6.523	95	6.528	100
67	6.263	37,64	6.430, 6.203	101,006
13	5.843	3	5.777	103
4	5.388	19	5.344	104
23	5.116	23	5.088	015
42	4.789	27.18	4.908, 4.765	105, 110
33	4.508	19	4.497	106
13	4.215	21	4.227	017
14	4.070	3	4.122	107
15	4.021	3	4.013	112
7	3.763	7, 29	3.779, 3.722	116, 0.0.10
15	3.550	19, 7	3.556, 3.548	019, 117
8	3.488	12	3.485	020
49	3.244	13, 28, 26, 12	3.264, 3.252, 3.233., 3.215	024, 201, 1.0.10, 202
91	3.062	22, 11, 73, 17, 14, 16	3.080, 3.074, 3.064, 3.044, 3.038, 3.033	204, 120, 121, 0.1.11, 026, 122
66	2.996	56, 11, 15	3.004, 2.989, 2.984	1.0.11, 205, 123
63	2.955	5, 28, 19, 7, 45	2.956, 2.947, 2.933, 2.919, 2.919	210, 211, 1.1.10, 212, 124
51	2.853	18, 7, 91, 13	2,889, 2.875, 2.842, 2.817	206, 213, 125, 214
60	2.763	100, 39, 19	2.759, 2.755, 2.747	1.1.11, 126, 215
18	2.676	19	2.668	216
7	2.599	5	2.599	1.1.12
8	2.193	21, 9, 4	2.191, 2.189, 2.183	1.0.16, 130, 1.2.12
5	2.070	5, 3, 1, 2	2.077, 2.074, 2.068, 2.064	310, 311, 0.0.18, 2.2.10
4	2.013	5, 5, 3, 4	2.027, 2.026, 2.014, 2.006	314, 039, 307, 2.2.10
3	1.950	8, 23, 3	1,970, 1.948, 1.935	316, 2.2.11, 0.2.16
5	1.892	11, 2, 3, 4, 3	1.900, 1.897, 1.894, 1.893, 1.889	2.1.15, 1.1.18, 2.0.16, 230, 2.2.12
7	1.848	12	1.846	320
5	1.811	4, 1, 8	1.814, 1,812, 1.810	3.1.10,1.1.19,236
2	i.776	1, 2	1.781, 1.7S9	3.0.12, 2.1.17
5	1.745	1, 3, 31, 1	1.747, 1.744, 1.743.1,739	2.0.18, 327, 040, 1.3.13
6	1.692	5, 12, 1	1.696, 1.692, 1.690	0.3.15, 0.0.22, 1.3.14
6	1.662	11, 2	1.664, 1.661	2.2.16.1.1.21
5	1.593	3, 2, 4, 2, 5	1.594, 1.594, 1.594, 1.593, 1.592	1.1.22, 405, 1.3.16, 0.3.17, 1.2.20
6	1.544	7	1.543	3.0.17
3	1.532	2	1.532	242
4	1.516	5	1.517	244

Table 2. X-ray powder diffraction data of günterblassite

* Calculated from structural data. The reflections with intensity ≥ 1 are given for the calculated X-ray powder diffraction pattern.

DISCUSSION

Günterblassite is not only a member of the new structural type, but the first known mineral with triplelayered tetrahedral SiO packet The discovery of this mineral outlines a special polysomatic series that links phyllosilicates and phylloaluminosilicates with tectosilicates. The degree of condensation of the tetrahedral (Si,Al)O motif progressively increases from the single-layer silicates of the mountainite family via double-layered silicates and aluminosilicates of the



Fig. 5. The structure of interlayer part of günterblassite. H_2O molecules occupy pendant (not shared with tetrahedra) apices of the Fe-polyhedron.

rhodesite series to günterblassite as a triple-layered aluminosilicate (Table 3). It can be supposed that a further increase in the number of layers will result in the formation of a 3D framework similar to those of feldspathoids, scapolites, and zeolites. Some minerals associated with günterblassite were altered to some extent. For example, the crystals of akermanite and götzenite are partially or completely replaced by X-ray amorphous hydrosilicates. The structural features of günterblassite (disordered large

Parameter	Shlykovite	Rhodesite	Günterblassite	
Formula	$K_2Ca_2[Si_8O_{18}(OH)_2] \cdot 6H_2O$	$\frac{\mathrm{HK}_{1-x}\mathrm{Na}_{x+2y}\mathrm{Ca}_{2-y}\times[\mathrm{Si}_{8}\mathrm{O}_{19}]\times}{(6-z)\mathrm{H}_{2}\mathrm{O}}$	$(K,Ca, Ba,Na,\Box)_3Fe[(Si,Al)_{13} \times O_{25}(OH.O)_4] \cdot 7H_2O$	
Symmetry, space group	Monoclinic, $P2_1/c$	Orthorhombic, Pmam	Orthorhombic, $Pnm2_1$	
Unit-cell dimensions				
a, Å	6.490	7.01-7.06	6.528	
$b, \mathrm{\AA}$	6.997	6.54–6.59	6.970 37.216 90	
<i>c</i> . Å	26.714	23.4-23.8*		
β, *	94.60	90		
$V, Å^2$	1209	1082-1098	1693.3	
Ζ	2	2	2	
Number of layers in the tetrahedral module	1	1	3.4	
Strong reflections of the	13.33–100	6.55–100	6.S85-45	
X-ray powder diffraction	6.67-76	6.30-32	6.523-100	
pattern: $a, A - I\%$	6.47–55	5.90-34	6.263–67	
	3469-45	5.032-28	4.789–42	
	3.068-57	4.386–47	3.244-49	
	3.042-45	2.864–25	3.062-91	
	2.945-62	2.762-23	2.996-66	
	2.912-90		2.955-63	
			2.853-51	
			2.763-60	
Density, g/cm ³	2.205 (calc)	2.27-2.36	2.18	
Optical data				
α	1.500	1.501-1.504	1.488	
β	1.509	1.505-1.508	1.490	
γ	1.515	1.513-1.518	1.493	
Optical sign, 2V	(–)60°	$(+)57-68^{\circ}$ (calc)	(+)80°	
Source	Pekov et al. (2011a)	Hesse et al 1992;	This study	
	Zubkova et al.2010	Mineraly (1992)		

Table 3.	Comparative	data of	f günterblassite	and related	mineral
Table 5.	Comparative	uata O	guineronassite	and related	mineran

* As for other minerals in this table, the rhodesite unit cell is given in the setting with Si layers coplanar to the *ab* plane.

cations, the sites of which are partially vacant, and high water content) and the similarity to the delhayelite-fivegite-hydrodelhayelite evolution series (Pekov et al., 2011a) indicate that günterblassite is a transformational mineral species formed as a result of the hydration and leaching of alkaline cations, Ca, and probably halogens from a hypothetic primary anhydrous cation-saturated mineral with the retention of the initial triple-layered aluminosilicate packet. The compromise growth surfaces between günterblassite and nepheline and leucite clearly indicate that the hypothetic anhydrous protophase of günterblassite crystallized simultaneously with these minerals. This protophase was most likely transformed into günterblassite at the low-temperature stage simultaneously with the crystallization of abundant zeolites. The significant content of barium in günterblassite may be caused by postcrystallization ion exchange.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (projects nos. 11-05-12001ofim-2011, 11-05-00407-a, 11-05-91331-NNIO_a).

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