= CHEMISTRY ====

Crystal Structure of Günterblassite, a New Mineral with a Triple Tetrahedral Layer

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Postmagmatic parageneses of the Eifel volcanic field (Germany) are characterized by a wide variety of minerals [1]. Günterblassite¹ is a new mineral discovered in a late association formed in the cavities of the alkaline basalt of the Rother Kopf mountain. The chemical composition was determined by electron

microprobe analysis. The content of H_2O was quantified by chromatographic analysis of gaseous products of calcination. The IR spectrum of the mineral shows the absence of borate, carbonate, nitrate, and ammonium groups. The empirical formula calculated for 13 atoms (Si, Al) is

$$Na_{0.14}K_{1.23}Ba_{0.30}Ca_{0.71}Mg_{0.16}Fe_{0.48}^{2+}[Si_{8.83}Al_{3.06}O_{24.17}(OH)_{4.83}] \cdot 7H_2O$$

(the hydrogen distribution between OH and H_2O was performed with allowance for the neutral formula).

Experimental X-ray diffraction data were collected in a full sphere of reciprocal space $(\sin\theta/\lambda < 0.45 \text{ Å}^{-1})$ from a block single crystal on an Oxford Diffraction Xcalibur diffractometer with a CCD detector. The crystal data and experimental details are summarized in Table 1. All calculations were performed with the AREN program package [2]. The structure of the cationic fragment was solved by direct methods, and the full model was determined by the phase correction procedure [3]. The structure was refined using 2706 non-averaged structure amplitudes $|F| > 2\sigma(F)$ because of the insufficient number of diffraction reflections. Some positions were refined using mixed atomic scattering curves.

After applying correction for absorption by the DIFABS program [4], the residual factor decreased to R = 4.9% in the anisotropic approximation. The final atomic coordinates and thermal parameters and site occupancy factors are presented in Table 2, and the composition and interatomic distances in the K and Fe polyhedra are listed in Table 3.

The günterblassite structure (Fig. 1) is based on a three-layer block consisting of three silicon–oxygen layers combined by shared vertices of Si tetrahedra. The outermost layers formulated as $[Si_4O_{10}]$ (Fig. 2a) differ from the middle $[Si_5O_{11}]$ layer, which contains an extra SiO₄ tetrahedron (Fig. 2b). The three-layer block has the $[Si_{13}O_{29}]^{6-}$ composition and is intermediate between the framework and layered silicon–oxygen motifs. In the block, there are channels running along [010] with effective cross-sections 3.1×3.8 and 3.8×4.8 Å in size and those running along [100], which are 4.0×4.3 and 4.3×4.4 Å in size.

¹ The mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, IMA No. 2011-032, on May 31, 2011.

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Table 1.	Crystal dat	a and experime	ent and refinem	ent details
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Idealized formula	$(K,Ca,Ba)_2(Fe,Ca,Mg,Na)(Si,Al)_{13}O_{25}(OH)_4 \cdot 7H_2O$				
Crystal system, space group, Z	Ortorhombic, <i>Pnm</i> 2 ₁ , 2				
a, Å	6.538(2)				
b, Å	6.975(2)				
<i>c</i> , Å	37.26(1)				
<i>V</i> , Å ³	1698.9(4)				
D_x , g/cm ³	2.22				
Radiation, λ , Å	$MoK_{lpha}, 0.71073$				
μ, cm ⁻¹	15.91				
Crystal size, mm	0.25 imes 0.2 imes 0.05				
Diffractometer	Xcalibur Oxford Diffraction, CCD detector				
Scan mode	ω				
θ_{max} , deg	19				
h, k, l ranges	$ \begin{array}{r} -5 < h < 6, -6 < k < 6, \\ -32 < l < 32 \end{array} $				
Number of reflections: measured/involved in refinement with $ F > 2\sigma(F)$	4092/2706				
Refinement method	Least squares on F				
Residual factor R_{aniso}	0.049				
Software	AREN [2], DIFABS [4]				

Tetrahedral blocks are combined by isolated Fe seven-vertex polyhedra with Fe–O distances of 2.38 (×2), 2.47(×2), 2.64, and $2.726(\times 2)$ Å. Between them, there are bulky ten-vertex polyhedra occupied by K

atoms. Another two atoms are located in the channels inside the tetrahedral blocks. The same channels accommodate seven water molecules surrounding the K atoms.

The crystal-chemical formula of günterblassite can be presented as (Z = 2)[K₁₂Ca₀₅Ba₀₃][Fe₀₅Ca₀₂Mg₀₁₅Na₀₁₅][(Si₁₀₃₅Al₂₆₅)O₂₅(OH)₄] · 7H₂O.

The OH groups and water molecules were identified by local bond valence sum calculations [5] for the corresponding oxygen positions.

The mineral has features in common with layered silicates of the mountainite—rhodesite family, for which the structure is based on corrugated layers with four- and eight-membered rings of silicon—oxygen tetrahedra in two orientations (Table 4).

Aqueous silicate K,Na,Ca-mountainite consists of single layers of $[Si_8O_{18}(O,OH)_2]$ composition and zigzag chains of edge-sharing $CaO_5(H_2O)$ octahedra located in the interlayer space. The K cations are in ten-vertex polyhedra located between the Ca octahedra. The space between the three-layer blocks is occupied by Na cations and H_2O molecules. The mountainite family includes shlykovite and cryptophyllite, which resemble mountainite in chemical composition and some structural features. Major differences between these minerals are in the shape of octahedral columns, which are zigzag in mountainite and straight in the other two minerals. The composition and arrangement of interlayer cations and water molecules in these structures are also different.

The mountainite layer can be considered as one half of the double layer of rhodesite and related minerals: macdonaldite, delhayelite, hydrodelhayelite, monteregianite-(Y), seidite-(Ce), and fivegite. These minerals, as well as some related synthetic silicates,

Atom	x/a	y/b	<i>z./c</i>	q	Q	B _{iso}
K1	0.072(1)	0	0.2279(5)	0.6	2	2.3(2)
K2	0.101(1)	0	0.0469(1)	0.8	2	1.2(2)
K3	0.229(2)	0.5	0.4225(1)	0.6	2	3.2(2)
Fe	0.246(2)	0.5	0.8685(2)	1	2	2.5(2)
Si1	0.384(1)	0	0.8211(1)	1	2	1.6(2)
Si2	0.199(1)	0.218(1)	0.3163(1)	1	4	1.7(2)
Si3	0.013(2)	0	0.7708(3)	1	2	2.6(3)
Si4	0.429(1)	0	0.6388(3)	1	2	1.1(3)
Si5	0.055(1)	0	0.6904(1)	1	2	1.0(3)
Si6	0.207(1)	0.221(1)	0.1400(2)	1	4	2.2(2)
Si7	0.028(1)	0	0.5774(5)	1	2	1.2(3)
Si8	0.047(2)	0	0.4915(3)	1	2	1.2(3)
Si9	0.210(1)	0.233(1)	0.9462(1)	1	4	2.0(2)
Si10	0.437(1)	0	0.4463(2)	1	2	1.2(2)
O 1	0.453(2)	0.316(2)	0.142(1)	1	4	1.7(4)
O2	0.240(2)	0	0.6060(4)	1	2	5.4(6)
O3	0.090(3)	0.323(3)	0.1777(5)	1	4	1.9(4)
O4	0.055(2)	0	0.7294(5)	1	2	3.1(6)
O5	0.052(1)	0.310(1)	0.1050(5)	1	4	2.2(4)
O6	0.225(6)	0	0.144(1)	1	2	1.7(5)
O 7	0.438(3)	0.311(2)	0.3228(3)	1	4	2.7(4)
O 8	0.260(2)	0	0.7830(2)	1	2	1.6(6)
O9	0.128(2)	0.316(2)	0.9838(3)	1	4	3.1(3)
O10	0.098(2)	0.289(1)	0.2823(3)	1	4	1.3(4)
O11	0.071(3)	0	0.5337(4)	1	2	3.8(5)
O12	0.263(3)	0	0.6696(5)	1	2	4.2(6)
O13	0.255(2)	0	0.4762(3)	1	2	1.7(5)
O14	0.181(4)	0	0.3231(6)	1	2	3.0(5)
O15	0.073(3)	0.294(2)	-0.0904(3)	1	4	4.3(4)
O16	0.450(2)	0.302(1)	-0.0593(3)	1	4	1.7(4)
O17	0.245(3)	0	-0.0466(4)	1	2	1.4(5)
OH1	0.251(1)	0	0.8570(2)	1	2	2.0(6)
OH2	0.058(1)	0.258(1)	0.3550(5)	1	4	3.4(4)
OH3	0.247(2)	0	0.4126(3)	1	2	3.7(5)
W1	0.245(4)	0.5	0.6207(5)	0.8	2	1.6(5)
W2	0.299(5)	0.5	0.798(8)	0.8	2	1.7(5)
W3	0.21(1)	0.5	0.495(1)	0.8	2	1.4(5)
W4	0.351(8)	0.5	0.697(1)	0.6	2	4.2(5)
W5	0.448(1)	0.259(2)	0.0450(1)	0.8	4	2.1(3)
W6	0.446(1)	0.261(1)	0.2281(3)	0.6	4	2.8(3)
<i>W</i> 7	0.443(3)	0.198(3)	0.3779(5)	0.6	4	5.7(1)

Table 2. Atomic coordinates, site multiplicity (Q) and occupancy (q), and isotropic parameters of atom displacements (B_{iso})

Position	Composition $(Z = 2)$	CN	Cation–anion distance, Å					
	Composition (2 - 2)		minimum	maximum	average			
K1	0.35K + 0.25Ca	8	2.86(1)	3.29(4)	2.99			
K2	$0.5 \mathrm{K} + 0.3 \mathrm{Ba}$	8	2.81(5)	3.22(1)	3.03			
K3	0.35 K + 0.25 Ca	10	2.68(5)	3.29(2)	3.03			
Fe	$0.5 \mathrm{Fe} + 0.2 \mathrm{Ca} + 0.15 \mathrm{Mg} + 0.15 \mathrm{Na}$	7	2.38(1)	2.726(8)	2.541			

 Table 3. Characteristics of the coordination polyhedra

constitute the rhodesite mero-plesiotype series. The structures of the members of this series are composed of double tetrahedral layers with the ratio T: O = 16: 38 resulting from fusion of two single mountainite layers through shared vertices of tetrahedra.

Comparison of the unit cells of the minerals listed in Table 4 shows that the a and b parameters, which are caused by the same layer topology, are close to or multiple of each other, while the c parameter changes depending on the thickness of the single, double, or



Fig. 1. Crystal structure of güunterblassite in projection along (a) [100] and (b) [010].



Fig. 2. (a) $[Si_4O_{10}]$ and (b) $[Si_5O_{11}]$ layers in the tetrahedral block of the günterblassite structure.

triple tetrahedral layer, as well as on the composition of the interblock space.

The topology of the *O* fragments of octahedra between tetrahedral layers in the minerals is also different. As distinct from mountainite, shlykovite, cryptophyllite, and rhodesite, the seidite-(Ce) structure contains single Ti octahedra. Analogously, the günterblassite structure contains isolated seven-vertex polyhedra of iron. Thus, the new mineral has some unique crystalchemical features, which distinguish it from the structurally studied minerals of this family. Günterblassite is the first member of a new structure type: it is a mineral with a triple tetrahedral layer. The existence of a mineral with a three-layer tetrahedral block (in addition to its one- and two-layer analogues) outlines a polysomatic series relating layered silicates and aluminosilicates to framework one (zeolites and feldspathoids).

Minoral	Formula		Unit cell	Space	Dafaranaa			
winiciai	ronnua	a, Å	b, Å	c, Å	β , deg	group	Reference	
Mountainite	$KNa_{2}Ca_{2}[Si_{8}O_{19}(OH)] \cdot 5H_{2}O$	6.58	13.70	13.75	105.75	<i>P</i> 2/ <i>c</i>	[6]	
Seidite-(Ce)	$\begin{array}{l} Na_{4}(Ce,Sr)_{2}\{Ti(OH)_{2} \\ [Si_{8}O_{18}]\}(O,OH,F)_{4} \\ \cdot 5H_{2}O \end{array}$	7.23	14.53	21.64	94.6	<i>C</i> 2/ <i>c</i>	[7]	
Rhodesite	$\text{KCa}_2[\text{Si}_8\text{O}_{18}(\text{OH})] \cdot 6\text{H}_2\text{O}$	6.56	7.05	23.42		Pmam	[8]	
Macdonaldite	$BaCa_{4}[Si_{8}O_{18}(OH)]_{2} \cdot 10H_{2}O$	13.11	14.08	23.56		Стст	[9]	
Hydrodelhayelite $KCa_2[AlSi_7O_{17}(OH)_2]_2F_2Cl$		6.65	7.07	23.85		$Pn2_1m$	[10]	
Monteregianite-(Y)	$KNa_2Y[Si_8O_{19}] \cdot 5H_2O$	9.51	9.62	23.96	93.85	$P2_{1}/n$	[11]	
Fivegite	$\begin{array}{l} K_4Ca_2[AlSi_7O_{17}(O_{2-x}OH_x)] \\ [(H_2O)_{2-x}OH_x]Cl \end{array} $	6.54	7.04	24.35		$Pm2_1n$	[12]	
Delhayelite	K ₄ Na ₂ Ca ₂ [AlSi ₇ O ₁₉] ₂ F ₂ Cl	6.58	7.06	24.58		Pmmn	[13]	
Shlykovite	$KCa[Si_4O_9(OH)] \cdot 3H_2O$	6.49	7.00	26.71	94.60	$P2_{1}/c$	[14]	
Cryptophyllite	$K_2Ca[Si_4O_{10}] \cdot 5H_2O$	6.49	6.99	32.09	94.68	$P2_{1}/n$	[14]	
Günterblassite	$\begin{array}{l}(K,Ca,Ba)_2(Fe,Ca,Mg,Na) \\ (Si,Al)_{13}O_{25}(OH)_4] \cdot 7H_2O\end{array}$	6.54	6.98	37.26		<i>Pnm</i> 2 ₁	This work	

Table 4.	Comparative	characteristics of	of related	minerals	based on	single,	double,	and tri	ple silicon-	-oxygen	layers
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Note: For uniformity, the unit cell parameters are given in common axis setting and in order of increasing *c* parameter. Space groups are given as in the corresponding original works.

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