

Parageorgbokiite, β - $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$, a New Mineral Species from Volcanic Exhalations, Kamchatka Peninsula, Russia¹

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Received April 12, 2005

Abstract—Parageorgbokiite, β - $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$, has been found at the second cinder cone of the Great Fissure Tolbachik Eruption, Kamchatka Peninsula, Russia. Ralstonite, tolbachite, melanothallite, chalcocyanite, euchlorine, Fe oxides, tenorite, native gold, sophite, Na, Ca, and Mg sulfates, cotunnite, and some copper oxoselenites are associated minerals. The estimated temperature of the mineral formation is 400–625°C. The color is green, with a vitreous luster; the streak is light green. The mineral is brittle, with the Mohs hardness ranging from 3 to 4. Cleavage is not observed. The calculated density is 4.70 g/cm³. Parageorgbokiite is biaxial (+); $\alpha = 2.05(1)$, $\beta = 2.05(1)$, and $\gamma = 2.08(1)$; $2V_{(\text{meas.})}$ is $\sim 0^\circ$, and $2V_{(\text{calc.})} = 0(5)^\circ$. The optical orientation is $X = a$; other details remain unclear. The mineral is pleochroic, from grass green on X and Y to yellowish green on Z . The empirical formula calculated on the basis of $\text{O} + \text{Cl} = 10$ is $\text{Cu}_{4.91}\text{Pb}_{0.02}\text{O}_{1.86}(\text{SeO}_3)_2\text{Cl}_{2.14}$. The simplified formula is $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$. Parageorgbokiite pertains to a new structural type of inorganic compounds. Its name points out its dimorphism with georgbokiite, which was named in honor of G.B. Bokii, the prominent Russian crystal chemist (1909–2000).

DOI: 10.1134/S1075701507070057

Parageorgbokiite, β - $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$, a new mineral species, was revealed as a single finding at the second cinder cone of the North breach of the Great Fissure Tolbachik Eruption (GFTE, 1975–1976, Kamchatka Peninsula, Russia). This mineral is associated with ralstonite; tolbachite; melanothallite; chalcocyanite; euchlorine; Fe oxides; tenorite; native gold; sophite; and Na, Ca, and Mg sulfates. Parageorgbokiite occurs as sporadic, slightly flattened dirty green transparent grains with a strong vitreous luster and is intergrown intimately with cotunnite and several natural copper oxoselenites, including ilinskite $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$ (Vergasova et al., 1997), chloromenite $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ (Vergasova et al., 1999a), burnsite $\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$ (Krivovichev et al., 2002), and allochalcoselite $\text{Cu}^+\text{Cu}_5^{2+}\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ (Vergasova et al., 2005). Parageorgbokiite crystallizes at a temperature ranging from 400 to 625°C.

This mineral is green, with light green streaking and a strong vitreous luster. It is brittle, with a Mohs hardness of 3 to 4. Cleavage is not observed. The calculated density is 4.70 g/cm³.

¹ Considered and recommended by the Commission on New Minerals and Mineral Names, Russian Mineralogical Society. Approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association, February 2, 2005.
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The optical properties were studied in highly refractive immersion liquids. Parageorgbokiite is biaxial and positive, with $\alpha = 2.05(1)$, $\beta = 2.05(1)$, and $\gamma = 2.08(1)$; $2V_{(\text{meas.})}$ is close to 0° , and $2V_{(\text{calc.})} = 0(5)^\circ$. The optical orientation is $X = a$; other details remain unclear. The mineral is pleochroic, from grass green on X and Y to yellowish green on Z .

The chemical composition of parageorgbokiite was studied with a Camebax SX-50 electron microprobe operating at 15 kV and 10 nA. Average results of 12 analyzed compositions and the standards used are presented in Table 1. The empirical formula calculated on the basis of $\text{O} + \text{Cl} = 10$ is $\text{Cu}_{4.91}\text{Pb}_{0.02}\text{O}_{1.86}(\text{SeO}_3)_2\text{Cl}_{2.14}$. The simplified formula is $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$.

Table 1. Chemical composition of parageorgbokiite, wt %

Component	Average	Range	Standard deviation	Standards used
CuO	57.98	56.94–59.33	0.66	Dolerophanite
PbO	0.66	0.00–1.49	0.41	PbS
SeO ₂	33.02	31.20–34.85	0.89	ZnSe
Cl	11.28	10.90–11.63	0.20	Chlorapatite
O=Cl ₂	–2.55	–2.4–2.62	0.04	
Total	100.39	98.25–101.81	1.16	

Table 2. XRD data for parageorgbokiite

hkl	d_{meas}	hkl	d_{theor}	hkl	hkl	d_{meas}	hkl	d_{theor}	hkl
30vw*	4.8	64	5.49	002	70	2.270	29	2.269	024
		28	5.33	100	60	2.117	15	2.123	221
		25	4.54	012	10	2.027	5	2.076	$\bar{1}33$
		11	4.44	110	40	1.953	9	1.946	213
		64	4.33	$\bar{1}11$	30	1.781	22	1.853	$\bar{2}24$
10	3.85	9	4.03	020			8	1.800	$\bar{2}15$
30	3.58	20	3.33	013			9	1.785	016
90	3.22	77	3.25	112	10	1.626	8	1.637	143
		49	3.17	$\bar{1}21$			6	1.615	302
100	3.01	100	3.01	121	20	1.580	5	1.584	$\bar{2}42$
20	2.78	30	2.746	004	30	1.521	9	1.517	151
80w**	2.61	14	2.664	200			6	1.499	322
		18	2.663	122	40	1.482	8	1.472	$\bar{1}45$
		17	2.656	113			8	1.467	$\bar{1}27$
		17	2.618	$\bar{1}04$			7	1.467	225
		24	2.608	031			5	1.462	027
40	2.58	14	2.564	$\bar{2}02$	40	1.406	8	1.421	243
		22	2.551	$\bar{2}11$	30	1.279	5	1.279	$\bar{4}21$
		54	2.540	$\bar{1}23$			3	1.270	$\bar{2}46$
20	2.42	19	2.443	$\bar{2}12$					

Notes: * Very broad line, ** broad line.

XRD data for parageorgbokiite were recorded from a small amount of material using a RKD camera 57.3 mm in diameter (CuK_α irradiation). The data were indexed from the calculated pattern and are shown in Table 2.

Single-crystal X-ray study was carried out with a Bruker SMART APEX CCD system at the Laboratory of Environmental Mineralogy and Crystal Structures, Notre Dame University, Indiana, the United States. The crystal structure was solved and refined to a final resid-

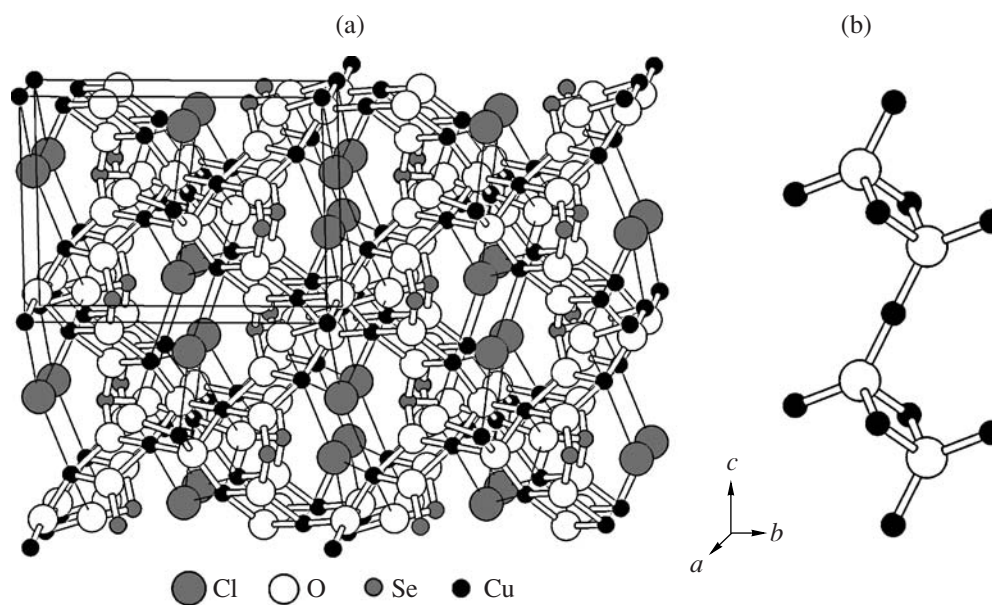


Fig. 1. (a) Structure of parageorgbokiite; (b) chain of oxocentered (OCu₄) tetrahedrons.

Table 3. Comparison of parageorgbokiite with georgbokiite

Parameter	Parageorgbokiite	Georgbokiite	Parameter	Parageorgbokiite	Georgbokiite
Formula	β -Cu ₅ O ₂ (SeO ₃) ₂ Cl ₂	α -Cu ₅ O ₂ (SeO ₃) ₂ Cl ₂	$V, \text{\AA}^3$	477.53(8)	462.3(6)
Symmetry	Monoclinic	Monoclinic	Z	2	2
Space group	$P2_1/c$	$P2_1/c$	$D_x, \text{g/cm}^3$	4.84	4.70
$a, \text{\AA}$	5.3982(5)	6.045(2)	Color	Chestnut brown	Green
$b, \text{\AA}$	8.0543(8)	13.778(2)	Streaking	Yellowish brown	Yellowish green
$c, \text{\AA}$	11.128(1)	5.579(5)	Optical sign	–	+
$\beta, ^\circ$	99.258(2)	95.76(4)	\bar{n}	2.11	2.06

ual value R of 0.033. Parageorgbokiite is monoclinic; space group $P2_1/c$; $a = 5.3982(5)$, $b = 8.0543(8)$, and $c = 11.128(1) \text{\AA}$; $\beta = 99.258(2)$; $V = 477.53(8) \text{\AA}^3$, $Z = 2$. The crystal structure of the mineral is presented in Fig. 1. Parageorgbokiite pertains to a new structural type of inorganic compounds. The structure consists of three symmetrically independent Cu atoms that are octahedrally coordinated by O²⁻ and Cl⁻ anions. The Jahn–Teller distortion (Jahn and Teller, 1937) common for Cu²⁺ minerals (Krivovichev et al., 2001) is characteristic of all octahedrons (Cu²⁺ ϕ_6 ; $\phi = \text{O, Cl}$). The structure is based on chains of oxocentered OCu₄⁶⁺ tetrahedrons, which are elongated along the a axis and connected alternately by apexes and edges. SeO₃²⁻ groups adjoin the tetrahedrons in the face-to-face mode (Krivovichev et al., 1999a; Krivovichev and Filatov, 2001) and form firm $\{[\text{O}_2\text{Cu}_5](\text{SeO}_3)_2\}^{2+}$ oxoselenite rods. These one-dimensional units are linked by Cu–O bonds to form a three-dimensional framework with Cl⁻ ions in its channels.

Parageorgbokiite is dimorphic with georgbokiite α -Cu₅O₂(SeO₃)₂Cl₂ (Vergasova et al., 1999b; Krivovichev et al., 1999b). The properties of parageorgbokiite compared with those of georgbokiite are shown in Table 3. Both minerals are monoclinic and belong to the same space group, $P2_1/c$. Moreover, the structures of these minerals have a common unit, an $\{[\text{O}_2\text{Cu}_5](\text{SeO}_3)_2\}^{2+}$ rod composed of oxocentered tetrahedrons and attached selenite groups. The structures are distinguished by the mode of organization of rods: in georgbokiite, they make up sheets that provide perfect cleavage parallel to (010), whereas, in parageorgbokiite, the rods form a three-dimensional framework. Transition between the two structural types is impossible without a radical topological rearrangement. The change in architecture of the structure results in replacement of the brown color of georgbokiite by the green color of parageorgbokiite.

Judging from abundances and the successful synthesis of georgbokiite by chemical transport reactions (Galy et al., 1979), georgbokiite is more stable than parageorgbokiite. However, the possibility and conditions of phase transition between the two modifications

remain unclear. Taking into account the larger volume of the unit cell and lower density of parageorgbokiite, it may be suggested that this mineral is a high-temperature modification of Cu₅O₂(SeO₃)₂Cl₂. Detailed study is necessary to reliably settle the problem.

The name of parageorgbokiite points out its dimorphism with georgbokiite, which was named in honor of G.B. Bokii (1909–2000), a corresponding member of the Russian Academy of Sciences and a prominent Russian crystal chemist.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project nos. 03-05-64853 and 06-05-64327) and the program “Development of the Scientific Potential of Higher Education Institutions” (project no. RNP 2.1.1.3077).

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