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## ON GERMANOCOLUSITE FROM KIPUSHI (KATANGA)

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Bornite from the Kipushi ore deposit was studied in Sample 64332 from the collection of the Fersman Mineralogical Museum. It was revealed to contain small oval inclusions of germanocolusite associated with renierite, tennantite, chalcopyrite, and sphalerite. Germanocolusite from Kipushi contains slightly more Zn and V and less As, as compared to germanocolusite from the type locality. A new crystallochemical formula proposed for germanocolusite takes into account the isomorphism  $\text{Zn}^{2+} + \text{Ge}^{4+} \rightarrow \text{As}^{5+} + \text{Cu}^+$ , characteristic for complex sulfides of Ge. This is the first find of germanocolusite at the Kipushi deposit. 5 tables and 7 references

Germanocolusite was approved as a mineral species in 1992 (Spiridonov *et al.*, 1992); but even earlier, «yellow germanites» were distinguished among germanites, in whose composition significant amounts of V and As were determined and which referred to as vanadium or vanadium – arsenic germanites. Spiridonov *et al.* (1992) demonstrated that varieties of the V or V – As germanites, in whose formulas Ge prevailed over As, represented germanocolusites. These researchers (Spiridonov *et al.*, 1992) presented 3 analyses of germanocolusite from the ore deposits Urup, Russia; Tsumeb, Namibia; and Chelopech, Bulgaria (Table 1, An. 1 – 3). Another analysis of a Ge sulfide from Urup, compositionally close to germanocolusite, was published by Kachalovskaya *et al.* (1975) and later repeated in the work by Spiridonov *et al.* (1986) under the name «colusite-Ge» (Table 1, An. 4). The concentration of Ge in this mineral exceeds that of As. The crystallochemical formula proposed for germanocolusite by Spiridonov *et al.* (1992) is as follows:  $\text{Cu}_{18}\text{Cu}^{2+}_4(\text{Cu}^{2+}, \text{Fe}, \text{Zn})_4\text{V}^{3+}_2\text{X}^{4+}_6\text{S}_{32}$ , where  $\text{X}^{4+} = \text{Ge}^{4+}, (\text{As}, \text{Sb}^{5+} + \text{As}, \text{Sb}^{3+}) : 2; \text{Sn}^{4+}, \text{Mo}^{4+}, \text{Te}^{4+}$ .

A recalculation of the germanocolusite analyses presented in the work (Spiridonov *et al.*, 1992) to this ideal formula revealed that 2 analyses from 3 ones were not electrically neutral (valence balances 4.2 and 3.5%) (Table 2, An. 1 and 3). Analyses are considered electrically neutral if their valence balances are no more than 3%. If to take into account the isomorphism  $\text{Ge}^{4+} + \text{Zn}^{2+} \rightarrow \text{As}^{5+} + \text{Cu}^+$ , characteristic for complex Ge sulfides, than the formula proposed by the discoverers can be presented as  $\text{Cu}^{+}_{18+x}\text{Cu}^{2+}_4(\text{Cu}^{2+}, \text{Fe}, \text{Zn})_{4-x}\text{V}^{3+}_2(\text{Ge}^{4+}_{6-x}\text{As}^{5+}_x)_6\text{S}_{32}$ , or  $\text{Cu}^{+}_{18+x}\text{Cu}^{2+}_4\text{Me}^{2+}_{4-x}\text{V}^{3+}_2(\text{Ge}^{4+}_{6-x}\text{As}^{5+}_x)_6\text{S}_{32}$ , where  $0 \leq x \leq 3$ . On recal-

culation to this formula, all analyses from the work (Spiridonov *et al.*, 1992) are electrically neutral (Table 2), which is evidence in favor of the formula that takes into account the isomorphous substitution  $\text{Ge}^{4+} + \text{Zn}^{2+} \rightarrow \text{As}^{5+} + \text{Cu}^+$ .

We found germanocolusite in Sample 64332 that was registered as bornite from the Kipushi (Katanga) ore deposit in the collection of the Fersman Mineralogical Museum. The germanocolusite is present as small oval grains up to 10 – 15  $\mu\text{m}$  in size, confined as a rule to renierite that, in its turn, is enclosed in bornite associated with tennantite, sphalerite, and chalcopyrite. Under reflected light, the germanocolusite is pinkish lilac, isotropic. The reflection intensity is lower than that of chalcopyrite and tennantite and higher than that of bornite and sphalerite. The particles are so fine that their X-ray identification is impossible.

The electron probe microanalysis was realized on a JEOL JXA-50A microprobe with a TRACOR-Xr energy-dispersive spectrometer (accelerating voltage 20 kV, beam current  $30 \cdot 10^{-9}$  A). The concentrations were calculated using the ZAF correction. The following standards (analytical lines) were used: ZnS ( $\text{Zn}_{K\alpha}$  and  $\text{S}_{K\alpha}$ ), GaAs ( $\text{As}_{K\alpha}$  and  $\text{Ga}_{K\alpha}$ ),  $\text{Cu}_2\text{FeSnS}_4$  ( $\text{Cu}_{K\alpha}$ ,  $\text{Fe}_{K\alpha}$ ,  $\text{Sn}_{L\alpha}$ ,  $\text{S}_{K\alpha}$ ), V and Ge metallic ( $\text{V}_{K\alpha}$ ,  $\text{Ge}_{K\alpha}$ ,  $\text{Ge}_{K\beta}$ ). The composition of germanocolusite from Kipushi is presented in Tables 3 and 4. A pronounced positive correlation is traced between Cu and As, also between Zn and Ge, and negative correlation is traced between Ge and As. All analyses calculated based on the formula taking into account the isomorphous substitution  $\text{Ge}^{4+} + \text{Zn}^{2+} \rightarrow \text{As}^{5+} + \text{Cu}^+$  are electrically neutral within the admissible range of 3%. As is seen from Table 5 that exhibits variations in the principal components of the germanocolusite composition, the

**Table 1. Electron microprobe analyses of germanocolusite: in wt. % (upper row) and in f.u. (lower row). (An. 1-3) after (Spiridonov *et al.*, 1992); (An. 4) after Kachalovskaya *et al.*, 1975**

№.	Element contents								Σ	Me/S
	Cu	Fe	Zn	Ge	As	Sb	V	S		
1	49.69	0.47	0.91	8.62	5.19	0.08	3.22	32.10	101.4	1.064
	24.96	0.27	0.44	3.79	2.21	0.02	2.02	31.96	66	
2	49.22	1.56	0.15	6.55	5.90	0.12	3.19	31.97	100.31	1.059
	24.91	0.90	0.07	2.90	2.53	0.03	2.01	32.06	65.99	
3	48.04	1.54	1.28	9.13	3.38	0.40	3.17	31.05	100.66	1.073
	24.50	0.89	0.63	4.08	1.46	0.11	2.02	31.39	65.99	
4	47.8	1.00	5.5	10.6	2.9		3.1	32.0	102.9	1.102
	23.66	0.56	2.65	4.59	1.22		1.91	31.40	65.99	

**Notes:** Trace elements: (An. 1): Sn 0.14% (0.04 f.u.), W 0.03 (0.01), Mo 0.67 (0.22), Ag 0.13 (0.04), and Bi 0.15 (0.02); (An. 2): Ga 0.35 (0.16), Sn 0.06 (0.02), W 0.06 (0.01), and Mo 1.18 (0.39); (An. 3): Ga 0.17 (0.08), Sn 0.17 (0.08), Ag 0.09 (0.03), and Se 1.08 (0.44). (An. 1 and 4) from the Urup deposit, (An. 2) from Tsumber, and (An. 3) from Chelovech

**Table 2. Recalculated germanocolusite analyses presented in Table 1**

№	Formulas calculated based on the ideal formula proposed by Spiridonov with co-authors (1992) $\text{Cu}^{+}_{18}\text{Cu}^{2+}_4(\text{Cu}^{2+}, \text{Fe}, \text{Zn})_4\text{V}^{3+}_2\text{X}^{4+}_{32}\text{S}_{32}$	Valence balance	
		±Δ	%
1	$(\text{Cu}^{+}_{18.00}\text{Ag}^{+}_{0.04})_{18.04}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{2.96}\text{Fe}^{2+}_{0.27}\text{Zn}_{0.44})_{3.67}(\text{V}^{3+}_{2.02}\text{W}^{4+}_{0.01}\text{Mo}^{3+}_{0.22})_{2.25}$ $[\text{Ge}^{4+}_{3.79}\text{Sn}^{4+}_{0.04}(\text{As}^{5+}_{2.21}\text{Sb}^{5+}_{0.02}\text{Bi}^{5+}_{0.02})_{2.25}]_{6.08}\text{S}_{31.96}$	+ 2.79	4.2
2	$\text{Cu}^{+}_{18}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{2.91}\text{Fe}^{2+}_{0.90}\text{Zn}_{0.07})_{3.88}(\text{V}^{3+}_{2.01}\text{W}^{4+}_{0.01}\text{Mo}^{3+}_{0.39})_{2.41}$ $[\text{Ge}^{4+}_{2.90}\text{Ga}^{3+}_{0.16}\text{Sn}^{4+}_{0.02}(\text{As}^{5+}_{2.53}\text{Sb}^{5+}_{0.03})_{2.56}]_{5.64}\text{S}_{32.09}$	-1.78	2.7
3	$(\text{Cu}^{+}_{18.00}\text{Ag}^{+}_{0.03})_{18.3}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{2.50}\text{Fe}^{2+}_{0.89}\text{Zn}_{0.63})_{4.02}\text{V}^{3+}_{2.02}$ $[\text{Ge}^{4+}_{4.08}\text{Ga}^{3+}_{0.08}\text{Sn}^{4+}_{0.36}(\text{As}^{5+}_{1.46}\text{Sb}^{5+}_{0.11})_{1.57}]_{6.09}(\text{S}_{31.39}\text{Se}_{0.44})_{31.83}$	+ 2.32	3.5
4	$\text{Cu}^{+}_{18}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{1.66}\text{Fe}^{2+}_{0.56}\text{Zn}_{2.63})_{4.87}\text{V}^{3+}_{1.91}$ $(\text{Ge}^{4+}_{4.59}\text{As}^{5+}_{1.22})_{5.81}\text{S}_{31.40}$ $\text{Cu}^{+}_{18}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{1.66}\text{Fe}^{2+}_{0.47}\text{Zn}_{2.63})_{4.78}(\text{V}^{3+}_{1.91}\text{Fe}^{3+}_{0.09})_{4.78}$ $(\text{Ge}^{4+}_{4.59}\text{As}^{5+}_{1.22})_{5.81}\text{S}_{31.40}$	+ 3.13	4.7
		+ 3.22	4.9
№	Formulas calculated based on the ideal formula $\text{Cu}^{+}_{18+x}\text{Cu}^{2+}_4\text{Me}^{2+}_{4-x}\text{V}^{3+}_2\text{Ge}^{4+}_6\text{As}_x\text{S}_{32}$	Valence balance	
		±Δ	%
1	$(\text{Cu}^{+}_{20.25}\text{Ag}^{+}_{0.04})_{20.29}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{0.71}\text{Fe}^{2+}_{0.27}\text{Zn}_{0.44})_{1.42}(\text{V}^{3+}_{2.02}\text{W}^{4+}_{0.01}\text{Mo}^{3+}_{0.22})_{2.25}$ $[\text{Ge}^{4+}_{3.79}\text{Sn}^{4+}_{0.04}(\text{As}^{5+}_{2.21}\text{Sb}^{5+}_{0.02}\text{Bi}^{5+}_{0.02})_{2.25}]_{6.08}\text{S}_{31.96}$	+ 0.53	0.8
2	$\text{Cu}^{+}_{20.56}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{0.33}\text{Fe}^{2+}_{0.90}\text{Zn}_{0.07})_{1.32}(\text{V}^{3+}_{2.01}\text{W}^{4+}_{0.01}\text{Mo}^{3+}_{0.39})_{2.41}$ $[\text{Ge}^{4+}_{2.90}\text{Ga}^{3+}_{0.16}\text{Sn}^{4+}_{0.02}(\text{As}^{5+}_{2.53}\text{Sb}^{5+}_{0.03})_{2.56}]_{5.64}\text{S}_{32.09}$	-0.78	1.2
3	$(\text{Cu}^{+}_{19.57}\text{Ag}^{+}_{0.03})_{19.6}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{0.93}\text{Fe}^{2+}_{0.89}\text{Zn}_{0.63})_{2.45}\text{V}^{3+}_{2.02}$ $[\text{Ge}^{4+}_{4.08}\text{Ga}^{3+}_{0.08}\text{Sn}^{4+}_{0.36}(\text{As}^{5+}_{1.46}\text{Sb}^{5+}_{0.11})_{1.57}]_{6.09}(\text{S}_{31.39}\text{Se}_{0.44})_{31.83}$	+ 0.75	1.2
4	$\text{Cu}^{+}_{19.22}\text{Cu}^{2+}_4(\text{Cu}^{2+}_{0.44}\text{Fe}^{2+}_{0.47}\text{Zn}_{2.63})_{3.56}(\text{V}^{3+}_{1.91}\text{Fe}^{3+}_{0.09})_{2.00}$ $(\text{Ge}^{4+}_{4.59}\text{As}^{5+}_{1.22})_{5.81}\text{S}_{31.40}$	+ 2.0	3.1

**Table 3. Electron microprobe analyses of germanocolusite from the Kipushi deposit (Sample 64332) in wt. % (upper row) and in f.u. (lower row)**

№	Element contents							Σ	Me/S
	Cu	Fe	Zn	Ge	As	V	S		
1	50.14	0.30	3.75	7.98	3.89	3.53	32.17	101.76	1.047
	24.96	0.17	1.82	3.48	1.64	2.19	31.74	66	
2	49.41	0.29	4.31	8.03	4.11	3.68	32.35	102.18	1.045
	24.49	0.16	2.08	3.48	1.73	2.28	31.78	66	
3	49.37	0.50	4.69	8.75	3.57	3.19	31.74	101.81	1.099
	24.68	0.28	2.28	3.82	1.52	1.98	31.44	66	
4	48.94	0.12	4.11	8.79	3.15	3.63	32.37	101.11	1.060
	24.45	0.07	2.00	3.84	1.34	2.26	32.04	66	
5	48.21	0.39	4.24	8.68	2.79	3.43	31.43	99.17	1.076
	24.61	0.22	2.10	3.88	1.21	2.18	31.79	65.99	
6	48.11	0.35	4.91	8.68	2.84	3.58	32.47	100.95	1.062
	24.03	0.20	2.38	3.80	1.20	2.23	32.15	65.99	
7	48.10	0.56	4.84	8.93	2.96	3.65	32.38	101.42	1.065
	23.96	0.32	2.34	3.89	1.25	2.27	31.96	65.99	
8	47.76	0.53	4.89	8.63	2.86	3.44	32.36	100.47	1.050
	23.97	0.30	2.38	3.79	1.22	2.15	32.18	65.99	
9	47.75	0.54	4.87	9.11	2.70	3.47	31.89	100.33	1.072
	24.08	0.31	2.39	4.02	1.16	2.18	31.86	66	
10	47.12	0.36	5.03	9.00	2.90	3.16	31.71	99.27	1.061
	24.01	0.21	2.49	4.05	1.25	2.00	32.02	66	

Table 4. Recalculated analyses of germanocolusite from the Kipushi deposit

№	Formulas calculated based on the ideal formula $\text{Cu}_{18+x}\text{Cu}_2\text{Me}^{2+}_{4-x}\text{V}^{3+}_2\text{Ge}^{4+}_{6-x}\text{As}_x\text{S}_{32}$	Valence balance	
		$\pm\Delta$	%
1	$\text{Cu}_{20.0}\text{Cu}_2(\text{Cu}^{2+}_{0.96}\text{Zn}_{1.82})_{2.78}(\text{V}^{3+}_{1.83}\text{Fe}^{3+}_{0.17})_{2.00}$ [Ge <sup>4+</sup> <sub>3.48</sub> (As <sup>5+</sup> <sub>1.64</sub> V <sup>5+</sup> <sub>0.36</sub> ) <sub>2.00</sub> ] <sub>5.48</sub> S <sub>31.74</sub>	0.0	0.0
2	$\text{Cu}_{20.17}\text{Cu}_2(\text{Cu}^{2+}_{0.32}\text{Zn}_{2.08})_{2.40}(\text{V}^{3+}_{1.84}\text{Fe}^{3+}_{0.16})_{2.00}$ [Ge <sup>4+</sup> <sub>3.48</sub> (As <sup>5+</sup> <sub>1.73</sub> V <sup>5+</sup> <sub>0.44</sub> ) <sub>2.17</sub> ] <sub>5.65</sub> S <sub>31.78</sub>	+ 0.18	0.3
3	$\text{Cu}_{19.78}\text{Cu}_2(\text{Cu}^{2+}_{0.90}\text{Zn}_{2.28})_{3.18}(\text{V}^{3+}_{1.72}\text{Fe}^{3+}_{0.28})_{2.00}$ [Ge <sup>4+</sup> <sub>3.82</sub> (As <sup>5+</sup> <sub>1.52</sub> V <sup>5+</sup> <sub>0.26</sub> ) <sub>1.78</sub> ] <sub>5.60</sub> S <sub>31.44</sub>	+ 1.44	2.2
4	$\text{Cu}_{19.67}\text{Cu}_2(\text{Cu}^{2+}_{0.78}\text{Zn}_{2.00})_{2.78}(\text{V}^{3+}_{1.93}\text{Fe}^{3+}_{0.07})_{2.00}$ [Ge <sup>4+</sup> <sub>3.84</sub> (As <sup>5+</sup> <sub>1.34</sub> V <sup>5+</sup> <sub>0.33</sub> ) <sub>1.67</sub> ] <sub>5.51</sub> S <sub>32.04</sub>	- 1.14	1.8
5	$\text{Cu}_{19.61}\text{Cu}_2(\text{Cu}^{2+}_{1.00}\text{Zn}_{2.10})_{3.10}(\text{V}^{3+}_{1.78}\text{Fe}^{3+}_{0.22})_{2.00}$ [Ge <sup>4+</sup> <sub>3.88</sub> (As <sup>5+</sup> <sub>1.21</sub> V <sup>5+</sup> <sub>0.40</sub> ) <sub>1.61</sub> ] <sub>5.49</sub> S <sub>31.79</sub>	- 0.2	0.3
6	$\text{Cu}_{19.63}\text{Cu}_2(\text{Cu}^{2+}_{0.40}\text{Zn}_{2.38})_{2.78}(\text{V}^{3+}_{1.80}\text{Fe}^{3+}_{0.20})_{2.00}$ [Ge <sup>4+</sup> <sub>3.80</sub> (As <sup>5+</sup> <sub>1.20</sub> V <sup>5+</sup> <sub>0.43</sub> ) <sub>1.63</sub> ] <sub>5.43</sub> S <sub>32.15</sub>	- 1.76	2.7
7	$\text{Cu}_{19.84}\text{Cu}_2(\text{Cu}^{2+}_{0.12}\text{Zn}_{2.34})_{2.46}(\text{V}^{3+}_{1.68}\text{Fe}^{3+}_{0.32})_{2.00}$ [Ge <sup>4+</sup> <sub>3.89</sub> (As <sup>5+</sup> <sub>1.25</sub> V <sup>5+</sup> <sub>0.59</sub> ) <sub>1.84</sub> ] <sub>5.73</sub> S <sub>31.96</sub>	- 0.4	0.6
8	$\text{Cu}_{19.67}\text{Cu}_2(\text{Cu}^{2+}_{0.30}\text{Zn}_{2.38})_{2.68}(\text{V}^{3+}_{1.70}\text{Fe}^{3+}_{0.30})_{2.00}$ [Ge <sup>4+</sup> <sub>3.79</sub> (As <sup>5+</sup> <sub>1.22</sub> V <sup>5+</sup> <sub>0.45</sub> ) <sub>1.67</sub> ] <sub>5.46</sub> S <sub>32.18</sub>	- 1.82	2.8
9	$\text{Cu}_{19.65}\text{Cu}_2(\text{Cu}^{2+}_{0.43}\text{Zn}_{2.39})_{2.82}(\text{V}^{3+}_{1.69}\text{Fe}^{3+}_{0.32})_{2.00}$ [Ge <sup>4+</sup> <sub>4.02</sub> (As <sup>5+</sup> <sub>1.16</sub> V <sup>5+</sup> <sub>0.49</sub> ) <sub>1.65</sub> ] <sub>5.67</sub> S <sub>31.86</sub>	- 0.1	0.2
10	$\text{Cu}_{19.46}\text{Cu}_2(\text{Cu}^{2+}_{0.55}\text{Zn}_{2.49})_{3.04}(\text{V}^{3+}_{1.79}\text{Fe}^{3+}_{0.21})_{2.00}$ [Ge <sup>4+</sup> <sub>4.02</sub> (As <sup>5+</sup> <sub>1.25</sub> V <sup>5+</sup> <sub>0.21</sub> ) <sub>1.46</sub> ] <sub>5.48</sub> S <sub>32.02</sub>	- 1.12	1.7
Formulas calculated on the ideal formula proposed by Spiridonov with co-authors, 1992 $\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}, \text{Fe}, \text{Zn})_4\text{V}^{3+}_2\text{X}^{4+}_6\text{S}_{32}$		Valence balance	
		$\pm\Delta$	%
1	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.96}\text{Fe}^{2+}_{0.17}\text{Zn}_{1.82})_{4.95}\text{V}^{3+}_{2.19}$ (Ge <sup>4+</sup> <sub>3.48</sub> As <sup>5+</sup> <sub>1.64</sub> ) <sub>5.12</sub> S <sub>31.74</sub>	+ 1.11	1.7
2	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.14}\text{Fe}^{2+}_{0.16}\text{Zn}_{2.04})_{4.34}\text{V}^{3+}_{2.24}$ (Ge <sup>4+</sup> <sub>3.44</sub> As <sup>5+</sup> <sub>1.70</sub> ) <sub>5.14</sub> S <sub>32.28</sub>	- 0.9	1.4
3	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.68}\text{Fe}^{2+}_{0.28}\text{Zn}_{2.28})_{5.24}\text{V}^{3+}_{1.98}$ (Ge <sup>4+</sup> <sub>3.82</sub> As <sup>5+</sup> <sub>1.52</sub> ) <sub>5.34</sub> S <sub>31.44</sub>	+ 2.42	3.7
4	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.45}\text{Fe}^{2+}_{0.07}\text{Zn}_{2.00})_{4.52}\text{V}^{3+}_{2.26}$ (Ge <sup>4+</sup> <sub>3.84</sub> As <sup>5+</sup> <sub>1.34</sub> ) <sub>5.18</sub> S <sub>32.04</sub>	- 0.2	0.3
5	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.61}\text{Fe}^{2+}_{0.22}\text{Zn}_{2.10})_{4.93}\text{V}^{3+}_{2.18}$ (Ge <sup>4+</sup> <sub>3.88</sub> As <sup>5+</sup> <sub>1.21</sub> ) <sub>5.09</sub> S <sub>31.79</sub>	+ 0.39	0.6
6	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.03}\text{Fe}^{2+}_{0.20}\text{Zn}_{2.38})_{4.61}\text{V}^{3+}_{2.23}$ (Ge <sup>4+</sup> <sub>3.80</sub> As <sup>5+</sup> <sub>1.20</sub> ) <sub>5.00</sub> S <sub>32.15</sub>	- 1.19	1.8
7	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{1.96}\text{Fe}^{2+}_{0.32}\text{Zn}_{2.34})_{4.62}\text{V}^{3+}_{2.27}$ (Ge <sup>4+</sup> <sub>3.89</sub> As <sup>5+</sup> <sub>1.25</sub> ) <sub>5.14</sub> S <sub>31.96</sub>	- 0.06	0.2
8	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{1.97}\text{Fe}^{2+}_{0.30}\text{Zn}_{2.38})_{4.65}\text{V}^{3+}_{2.15}$ (Ge <sup>4+</sup> <sub>3.79</sub> As <sup>5+</sup> <sub>1.22</sub> ) <sub>5.01</sub> S <sub>32.18</sub>	- 1.35	2.0
9	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.08}\text{Fe}^{2+}_{0.31}\text{Zn}_{2.39})_{4.78}\text{V}^{3+}_{2.18}$ (Ge <sup>4+</sup> <sub>4.02</sub> As <sup>5+</sup> <sub>1.16</sub> ) <sub>5.18</sub> S <sub>31.86</sub>	+ 0.98	1.5
10	$\text{Cu}_{18}\text{Cu}_2(\text{Cu}^{2+}_{2.01}\text{Fe}^{2+}_{0.21}\text{Zn}_{2.49})_{4.71}\text{V}^{3+}_{2.00}$ (Ge <sup>4+</sup> <sub>4.02</sub> As <sup>5+</sup> <sub>1.25</sub> ) <sub>5.27</sub> S <sub>32.02</sub>	- 0.54	1.6

Table 5. Variations in the concentrations of the principal elements (in wt. %) in germanocolusite: (1) from the Kipushi deposit and (2) from the Urup, Tsumeb, and Chelopech deposits

Element	1	2
Cu	47.12 – 50.14	48.04 – 49.69
Fe	0.12 – 0.56	0.47 – 1.56
Zn	3.75 – 5.03	0.07 – 0.63
Ge	7.98 – 9.11	6.55 – 9.13
As	2.70 – 4.11	3.38 – 5.90
V	3.16 – 3.68	3.17 – 3.22
S	31.43 – 32.38	31.05 – 32.02

analyses of germanocolusite from the Kipushi deposit contains more Zn, less As, slightly more Ge, and less Fe, as compared to analyses of germanocolusite from the Urup, Tsumeb, and Chelopech deposits. The average analysis of 10 analyses of germanocolusite from Kipushi does not completely correspond to the crystallochemical formula that takes into account the isomorphism  $\text{Ge}^{4+} + \text{Zn}^{2+} \rightarrow \text{As}^{5+} + \text{Cu}^{+}$ :  $\text{Cu}^{+}_{19.75}\text{Cu}^{2+}_{4.0}(\text{Cu}^{2+}_{0.60}\text{Zn}_{2.22})_{2.82}(\text{Fe}^{3+}, \text{V}^{3+})_2[\text{Ge}^{4+}_{3.80}(\text{As}^{5+}_{1.35}\text{V}^{5+}_{0.40})_{1.75}]_{5.55}\text{S}_{31.90}$ , or  $\text{Cu}^{+}_{19.8}\text{Cu}^{2+}_{4.0}(\text{Cu}^{2+}_{0.6}\text{Zn}_{2.2})_{2.8}(\text{Fe}^{3+}, \text{V}^{3+})_2[\text{Ge}^{4+}_{3.8}(\text{As}^{5+}_{1.4}\text{V}^{5+}_{0.4})_{1.8}]_{5.6}\text{S}_{32}$ . The number of divalent cations is more and the sum of 4- and 5-valence cations is less by approximately the same value, than it is required according to this crystallochemical formula. It is probable that some of the divalent cations occupy positions of the 4- and 5-valence ones; that is, the isomorphism is more complicated. This assumption is based on investigation of the Fe position in renierite, using the Mössbauer spectroscopy. It was revealed that Fe occupied three different positions (Bernstein *et al.*, 1989). The same was confirmed by studying the renierite structure using the Rietveld method (Bernstein *et al.*, 1989). In this case, the crystallochemical formula of germanocolusite will as follows:  $\text{Cu}^{+}_{18+x}\text{Cu}^{2+}_4\text{Me}^{2+}_{4-x}\text{Me}^{3+}_2[\text{Me}^{4+}_{6-x-y}\text{Me}^{5+}_x\text{Me}^{2+y}]_6\text{S}_{32}$ , where  $\text{Me}^{2+}$  is  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ;  $\text{Me}^{3+}$  is  $\text{V}^{3+}$ ,  $\text{Fe}^{3+}$ ;  $\text{Me}^{4+}$  is  $\text{Ge}^{4+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ga}^{3+}$ ;  $\text{Me}^{5+}$  is  $\text{As}^{5+}$ ,  $\text{V}^{5+}$ ,  $\text{Sb}^{5+}$ ,  $\text{Bi}^{5+}$ ; at  $0 \leq x \leq 3.0$  and  $0 \leq y \leq 0.5$ .

An examination of the literature data has demonstrated that none analysis of germanite or colusite from the Kipushi deposit has been published until the present. Germanium mineralization of Kipushi was studied by Viaene and Morean (Viaene *et al.*, 1968). From among Ge-containing sulfides, they found briartite and renierite only. They noted neither germanite nor Ge-containing colusite. In his work on renierite, Bernstein (1986) placed germanite from the Kipushi deposit into the table; however, describing mineral assemblages of this

deposit, he noted none Ge sulfides except for renierite. In *Geological handbook on siderophile and chalcophile rare metals* (1989), mention is made of the fact that renierite only is present at Kipushi. It seems likely that our find of germanocolusite is the first for the Kipushi deposit.

## References

- Bernstein L.R. Renierite,  $\text{Cu}_{10}\text{ZnGe}_2\text{Fe}_4\text{S}_{16}$  —  $\text{Cu}_{11}\text{GeAsFe}_4\text{S}_{16}$  a coupled solid solution series. // *Amer. Mineral.*, **1986**, vol. 71, p. 210-221.
- Bernstein L.R., Reichel D.G., Merlino S. Renierite crystal structure from Rietveld analysis of powder neutron — diffraction data. // *Amer. Mineral.*, **1989**, vol. 74, p. 1177-1181.
- Geologicheskii spravochnik po siderofilnym i khalkofilnym redkim metallam (Geological handbook on siderophile and chalcophile rare metals). N.P. Laverov, Ed. // Moscow: Nedra, **1989**. (Rus.)
- Kachalovskaya V.M., Osipov B.S., Kukoev V.A., Kozlova E.V. Germaniy sodержashchie mineraly iz bornitovykh rud mestorozhdeniya Urup (Germanium-containing minerals from bornite ores of the Urup deposit) // *Zap. Vses. Min. O-va*, **1975**, part 104, no. 1, pp. 94 — 97. (Rus.)
- Spiridonov E.M., Kachalovskaya V.M., Badalov A.S. Rasnovidnosti kolusita, o vanadievom i vanadievo-mysh'yakovom germanite (Varieties of colusite and on vanadium and vanadium — arsenic germanite). // *Vestn. Mosk. Univ.*, **1986**, Ser. Geol., no. 3, pp. 60 — 68. (Rus.)
- Spiridonov E.M., Kachalovskaya V.M., Kovachev V.V., Krapiva L.Ya. Germanokolusit  $\text{Cu}_{26}\text{V}_2(\text{Ge}, \text{As})_6\text{S}_{32}$  — novyi mineral. (Germanocolusite,  $\text{Cu}_{26}\text{V}_2(\text{Ge}, \text{As})_6\text{S}_{32}$ , a new mineral). // *Vestn. Mosk. Univ.*, **1992**, Ser. Geol., no. 6, pp. 50 — 54. (Rus.)
- Viaene W., Morean J. Contribution a l'etude de la germanite, de la renierite et de la briartite. // *Ann. De la Societe Geologique de Belgique*. **1968**, n. 91, p. 127 — 143.