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NEW DATA ON GALKHAITE

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The chemical composition of galkhaite from several deposits (Gal-Khaya, Yakutia, Russia; Khaidarkan, Chauvay, Kyrgyzstan; Getchell, Nevada, U.S.A.) was studied using the electron microprobe. Galkhaite from all these deposits contains species-forming Cs $(3.6-6.6$ wt %) prevailing over thallium (Cs > Tl) in all samples. The mineral from Khaidarkan contains up to 1.0 wt.%, from Chauvay — up to 2.9% Ag. Contents of Na, K, Rb, Ca, Sr, Ba, Pb, Cd, Fe, Se, Te in all the studied samples were below detection limits. It is suggested that the empirical formula of galkhaite be calculated on the basis of the sum: $(Hg + Cu + Zn + Fe + Ag + As + Sb + S) = 22$. The (Cs,Tl) occupancy is $50-100\%$, and that suggests the refined idealized formula of galkhaite: $(Cs,Tl)_{0.5-1} (Hg,Cu,Zn)_6(As,Sb)_4S_{12}$. The influence of conditions of the microprobe analysis on the results for galkhaite and the crystallochemical reason of strong affinity of the mineral to cesium, the indicator role of galkhaite as related to the Cs geochemistry are discussed. The concentration of cesium in the process of formation of hydrothermal arsenic-antimony-mercury mineralization is the main factor limiting the amount of galkhaite crystallized, so that Cs activity may determine the types of mercury ore.

2 tables, 18 references.

Galkhaite, $(Cs,Tl)(Hg,Cu,Zn)_6(As,Sb)_4S_{12}$, is typical mineral of some low-temperature hydrothermal ore deposits. For the first time for natural sulfides, the species-forming role of cesium and the Cs-Tl isomorphism have been revealed in galkhaite. It is just these crystal-chemical features of the mineral that attracted our attention. The history of the study of galkhaite is rather short — not more than 30 years but quite complicated, its formula and crystal structure have been refined more than once. Galkhaite was first described in 1972 at the arsenic-antimony-mercury deposits Gal-Khaya (Yakutia) and Khaidarkan (Kyrgyzstan) simultaneously, whereas in the Khaidarkan ore field the mineral had been found in more than ten localities, in several ore types. According to the wet chemical analysis data (Table 1, an. 1, 2), Gruzdev and co-authors (1972) suggested for the mineral an idealized formula of $HgAsS_2$.

A year later, galkhaite was found at the Getchell gold deposit, Nevada, U.S.A. In the publication about that find, the authors "enlarged" the idealized formula of the mineral to include secondary components: $(Hg,Cu,Tl,Zn)(As,Sb)S_2$ (Botinelly et al., 1973); data on galkhaite from the Getchell mine was also published by Jungles (1974).

In 1975, two papers on the crystal structure of the mineral were published independently. Kaplunnik et al. (1975), having studied a single crystal from the Gal-Khaya deposit and using data on the mineral composition published by Gruzdev et al. (1972) — (Table 1, an. 1) — revealed the structural similarity of galkhaite and fahlore and confirmed the formula $HgAsS_2$. Divjakovic and Nowacki (1975) investigated a single crystal from the Getchell mine and detected in the galkhaite structure a site occupied by a heavy element surrounded by 12 atoms of sulfur, which had not been found by Kaplunnik et al. (1975). Basing of the chemical composition determined using the spectrographic method by Botinelly et al. (1973) — (Table 1, an. 4), V. Divjakovic and W. Nowacki concluded that the site was occupied by thallium, a bit less than a half. They suggested for the studied sample the following formula: $[Hg_{0.76}(Cu,Zn)_{0.24}]_{12}$ $Tl_{0.96}(AsS_3)_8$. The crystal structure was refined to an R index of 4.5% based on 132 observed unique reflections (Divjakovic, Nowacki, 1975), whereas in the paper by Kaplunnik et al. (1975) the final value of an R index is 9.8% for 122 unique reflections. For that reason, the model proposed by V. Divjakovic and W. Nowacki was concluded to be more correct (Chen, Szymanski, 1981).

T.T. Chen and J.T. Szymanski performed the microprobe study of 47 galkhaite crystals from the Getchell mine, obtained from different sources; they found that all of the crystals contain cesium in significant amount $(3.7-7.1$ wt.% Cs) (Table 1, an. $7-8$). These authors studied the structure of a crystal ($R = 2.64\%$ for 680 unique reflections) and revealed that Cs atoms, together with Tl, occupy the site, found by V. Divjakovic and W. Nowacki, in the 12-fold polyhedron formed by S atoms, and, in all cases studied, Cs > Tl. A small amount of Tl was also fixed in a site occupied by Hg, Cu and Zn. This fact explains clearly the great deficiency of thallium in the model proposed by V. Divjakovic and W. Nowacki, based upon analyses with the missed cesium (consequently, previously, the model had not considered the presence of the lighter atoms in the 12-fold polyhedron "Tl"). That allowed T.T. Chen and J.T. Szymanski to refine the idealized formula of galkhaite as the following: $(Hg,Cu,Zn,Tl,Fe,\square)_6(Cs,Tl,\square)(As,Sb)_4$

Table 1. **Chemical composition of galkhaite: the earlier published data**

Constituents	1	2	3	4	5	6	7	8
				wt %				
Cs			3.3			5.6	5.1	3.7–7.1
Tl	0.46	2.90	0.8	5	3.5	3.0	2.4	b.d.l.–4.2
Hg	47.60	49.02	51.9	42	50.2	50.0	50.7	48.3–53.0
Cu	3.49	2.85	3.3	5	3.4	3.3	3.2	1.6–3.6
Zn	3.00	0.60	1.6	1.5	1.2	1.5	1.8	0.3–2.5
Fe	0.31	b.d.l.	b.d.l.	0.7		b.d.l.	0.1	b.d.l.–0.5
As	23.60	19.49	14.4	24	15.8	15.8	15.2	14.5–15.9
Sb	0.59	5.51	3.1	0.3		b.d.l.	0.3	b.d.l.–3.1
S	21.00	19.31	22.3	21.3*	22.6	22.1	22.0	20.9–22.7
Se	0.0003	0.015						
Total	100.05	99.695	100.7	99.8*	96.7	101.3	100.8	99.9–101.8
	Formula calculated on (Hg + Cu + Zn + Fe + As + Sb + S) = 22							
Cs			0.44			0.76	0.69	
Tl	0.04	0.26	0.07	0.41	0.30	0.26	0.21	
Σ(Cs,Tl)	(0.04)	(0.26)	0.51	(0.41)	(0.30)	1.02	0.90	
Hg	3.96	4.46	4.56	3.51	4.45	4.48	4.54	
Cu	0.915	0.82	0.915	1.32	0.95	0.93	0.91	
Zn	0.765	0.165	0.43	0.39	0.325	0.41	0.495	
Fe	0.09	–	–	0.21		–	0.03	
Σ(Hg,Cu,Zn,Fe)	5.73	5.445	5.905	5.43	(5.725)	5.82	5.975	
As	5.26	4.745	3.385	5.38	3.75	3.79	3.65	
Sb	0.08	0.825	0.45	0.04		–	0.045	
Σ(As,Sb)	5.34	5.57	3.835	5.42	(3.75)	3.79	3.695	
S	10.93	10.985	12.26	11.15*	12.525	12.39	12.33	

Notes: b.d.l. – below detection limit; empty cell means absence of data; sums in parentheses are given for analyses where one of the sum components was not detected.
1 – Gal-Khaya, wet chemical data (Gruzdev et al., 1972);
2 – Khaidarkan, wet chemical data (Gruzdev et al., 1972);
3 – Khaidarkan, electron microprobe data, average for 3 analyses (Chen, Szyman'ski, 1982);
4 – Getchell, spectrographic data; minor admixtures of Al, Cd, Ag, Ca, Mg, Mn are also revealed – summary 0.2 wt. %;
5 – Getchell, electron microprobe data (Botinelly et al., 1973);
6 – Getchell, electron microprobe data (Chen, Szyman'ski, 1982);
7 – Getchell, electron microprobe data, average for 21 analyses (Chen, Szyman'ski, 1981);
8 – Getchell, electron microprobe data, ranges for 21 analyses (Chen, Szyman'ski, 1981).
* – content of S calculated from the analytical sum deficiency (Botinelly et al., 1973);

S_{12}. There were distinguished, in the structure of this sulfosalt, the AsS_3 trigonal pyramids, HgS_4 tetrahedra centered by mercury atoms, and the Laves 12-fold polyhedron CsS_{12} (Chen, Szymański, 1981). A year later, the same authors carried out an additional study of a galkhaite sample from Khaidarkan (Table 1, an. 3), they showed that it also contains cesium (3.2 – 3.4 wt.% Cs), and that Cs > Tl. For a comparison, the additional analysis of a crystal from the Getchell mine was made in the same conditions (Table 1, an. 6) (Chen, Szymański, 1982). It should be noted that all the structural investigations have supported the space group $I - 43m$ firstly reported for galkhaite by Gruzdev et al. (1972).

To date, the number of galkhaite finds has increased. For instance, in Nevada, apart from the Getchell mine, it has been found in gold ore deposits at Carlin (Radtke et al., 1978), Elko Canyon, Goldstrike and Rodeo (Castor, Ferdock, 2004). The mineral was also described in the gold deposit at Hemlo, Ontario, Canada (Robinson, 1986), and detected in Zashuran, Iran (Mehrabi et al., 1999). Specimens of galkhaite from the Chauvay mercury deposit, Kyrgyzstan, take place in many collections, but the data on chemical composition of the mineral from Chauvay were not published.

As a rule, galkhaite occurs in the veined ores where it is associated with fluorite, quartz, calcite, pyrite, and various Hg, Sb and As sulfides: cinnabar, metacinnabar, stibnite, realgar, orpiment, getchellite, wakabayashilite, aktashite, etc. On the whole, galkhaite is a rare; only in two deposits, namely Getchell (Tretbar et al., 2000) and Chauvay, it is widespread. According to unpublished data of V.Yu. Volgin, in some areas

of the Chauvay deposit, galkhaite appears to be the principal mercury-bearing ore mineral.

We used the electron microprobe method to study the chemical composition of galkhaite from Gal-Khaya, Chauvay, Khaidarkan, and, for comparison, under the same conditions, from the Getchell mine. This work is caused by several reasons. First of all, there was absent, hitherto data about the content of cesium in galkhaite from Gal-Khaya deposit; correcting this omission seemed very important because the first analysis of this mineral had shown the low Tl content — 0.46 wt.% (Gruzdev et al., 1972), and a site with large heavy atoms, occupied by Cs and Tl in studied galkhaite from Getchell, was not found in its structure, (Kaplunnik et al., 1975). Both these two facts evoked the question: had cesium been missed in the first investigation of the mineral from Gal-Khaya, or does the holotype galkhaite differs principally from this, well-studied mineral from Getchell? Secondly, it looked quite interesting to further investigate the compositions of galkhaite from Chauvay, where it is among principal components of mercury ores, and from different blocks of the large Khaidarkan ore field.

The new impulse of interest for galkhaite has been brought about by one other aspect — the close geochemical link that had been revealed between Cs (and Rb) and potassium-bearing sulfides in derivatives of agpaitic alkaline massifs. This link was known long ago for thallium, but recently the data appeared concerning significant enrichment of representatives of the rasvumite (KFe_2S_3) structural type, in heavy alkali metals: Rb (up to 7.4 wt.%) and Cs (up to 2.9%) were reported in rasvumite from the peralkaline rocks of the Mont Saint-Hilaire complex, Quebec, Canada (Chakhmouradian et al., 2001), and the Cs-analog of rasvumite — pautovite, $CsFe_2S_3$, was discovered in the Lovozero alkaline complex, Kola Peninsula, Russia. This new mineral contains 36.1 wt.% Cs, 1.3% Rb, 0.5% Tl and 0.2% K — it is one of the richest in cesium natural compounds (Pekov et al., 2005).

Therefore, the Tl-Cs-sulfide — galkhaite has become quite an interesting object to investigate regarding the possible entering of Rb, K and some other large atoms in chalcogenide minerals formed in the "classic-type" ore deposits. Seven samples were studied; their brief description is given below.

#2046: Gal-Khaya, Yakutia. Well-shaped cubic, dark orange crystals of galkhaite, with edges up to 1 mm, from a carbonate vein in black shist. Specimen no. 73879 in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, deposited in 1971 by V.S. Gruzdev as the type specimen.

#2047: Getchell, Nevada. Well-shaped cubic, dark orange-red crystals of galkhaite, with edges up to 3 mm, from a cavity in quartz vein. Specimen no. 90510 in the systematic collection of the Fersman Mineralogical Museum.

#2048: Kara-Archa area, Khaidarkan, Kyrgyzstan. orange-brown grains of galkhaite up to 3 mm in size; from a quartz, with getchellite, veinlet in black shale. Sample № 73879 in systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences.

#2049: Khaidarkan, Kyrgyzstan. Bright orange cubic crystals and grains of galkhaite, up to 1.5 mm in size, in the brecciated quartz-fluorite aggregate. Specimen from the collection of I.V. Pekov, received from V.Yu. Volgin.

#2050: Chauvay, Kyrgyzstan. Crude orange cubic crystals of galkhaite, up to 1 cm in size, in a quartz veinlet cross-cutting black shist, with stibnite, cinnabar and aktashite. Specimen from the collection of I.V. Pekov, received from V.Yu. Volgin.

#2051: Chauvay, Kyrgyzstan. Rich aggregates of dark orange grains of galkhaite, up to 5 cm across, in quartz veinlets cross-cutting black shist, with a small amounts of cinnabar and stibnite. Specimen from the reference collection of the Fersman Mineralogical Museum.

#2052: Chauvay, Kyrgyzstan. Bright orange cubic crystals of galkhaite, up to 1 mm in size, ingrown into fluorite and gypsum in cavities of a quartz veinlet. Specimen from the collection of I.V. Pekov, received from V.I. Vasil'ev.

Analyses were carried out on the polished section of galkhaite grains mounted into solidified epoxy resin. The wave-dispersion mode was used with a Camebax SX 50 istrument (analyst I.A. Bryzgalov). The work, in its process, was impacted by a series of methodical problems, which forced, more than once, repeated analyses, before adjusting to conditions so that reproducible results could be obtained. One of the problems concerned the overlaps of analytical lines, of the whole scope of elements, typically used in the analysis of sulfides. It was caused by the unusual chemical composition of galkhaite including, together and in large amounts, sulfur and the heavy elements — Hg, As, Tl, Cs. This factor placed some restrictions on the standards to be used and forced the using for Tl determination the unusual line $M\beta$, and for As — $K\alpha$.

For elements present in galkhaite in amounts exceeding the detection limits, the optimal complex of analytical lines and stan-

dards used the following: $CsL\alpha$ $-CsLaPO_4$, $TlM\beta - TlAsS_2$, $HgL\alpha - HgTe$, $CuK\alpha -- CuSbS_2$, $ZnK\alpha -- ZnSe$, $AgL\alpha - AgAsS_2$, $AsK\alpha - FeAsS$, $SbL\alpha -- Sb_2S_3$, $SK\alpha - Bi_2S_3$. Operating voltage $-$ 20 kV, beam current $-$ 30 nA, beam area 10×10 μm^2, time of the signal ascent on the peak $-$ 10 seconds, on the background $-$ by 5 seconds, on each side.

Galkhaite has proved to be stable under electron beam: neither melting nor cracking ("burning out") were observed; there was only noted, in the point of analysis, some "swelling" of the carbon film coating the sample surface for electric conductivity. Meanwhile, empirically it has been revealed that the results of this mineral analysis depended strongly on the thickness of the carbon film. With film too thin, the overstatement of the analytical sum was usually $(103 - 109$ wt.%), with significant "distortion" of the components ratios, first of all with strong overstatement of the measured Hg content. On the contrary, film too thick brought the significant decrease of the analytical sum: down to $87 - 93$ wt.%. The results were also strongly affected by the difference in thickness between films on galkhaite and the standard samples; the best method was to avoid the simultaneous spray-coating on standard and the studied samples. Note that the results of the analyses of other mercury minerals $-$ cinnabar and aktashite, mounted in the epoxy resin together with galkhaite, showed no dependence on the film thickness.

Stable results were obtained in analyses of galkhaite with the sums being within limits $101 - 102$ wt.%; correctness of the data is confirmed by the fact that, calculated on their base, formula indices for S and $\Sigma(Hg,Cu,Zn,Ag)$ in structurally caused formula $(Cs,Tl)(Hg,Cu,Zn)_6$ $(As,Sb)_4S_{12}$ deviate from the whole numbers by no more than 3 rel.%, and for $\Sigma(As,Sb)$ $-$ by no more than 5 rel.% (Table 2).

There were 4 analyses obtained for each specimen. The contents of each constituent varied at different points within the sample by no more than 1.5 rel.%. No chemical zoning in galkhaite crystals was observed. Typical compositions are shown in Table 2. The contents of Na, K, Rb, Ca, Sr, Ba, Pb, Cd, Fe, Se and Te in all specimens turned out to be below detection limits. We attribute excess of the analysis sums over 100 wt.% to the above mentioned effect of the carbon film thickness. It should be noted that the sums over 102 wt.% in electron microprobe analyses of galkhaite has been indicated by Chen and Szymański (1981); they believed its reason to be connected to the possible overlap of analytical lines when not quite appropriate standards were uesd.

We have compared several ways to calculate the empirical formula of galkhaite. The optimal one, taking into account the random errors in the determination of all components, has become the calculation on the sum $(Hg + Cu + Zn + Fe + Ag + As + Sb + S) = 22$. Cs and Tl aren't included in the basis of calculation because the (Cs,Tl) site may be partially vacant (see below). Besides our data (Table 2), the previously published analyses of galkhaite were also recalculated in the same way (Table 1). The comparison of the obtained formulae shows that all electron microprobe analyses of galkhaite from different localities, both our and early reported ones, are on the whole quite close to one another and correspond well to the crystal structure data for the mineral from the Getchell mine (Divjaković, Nowacki, 1975; Chen, Szymański, 1981).

At the same time, chemical (Table 1, an. $1 - 2$) and spectrographic (Table 1, an. 4) data demonstrate the significantly higher content of As and the lower content of S in comparison to the theoretical values. Comparing the results of electron microprobe analyses among them, it should be mentioned that our analyses are firmly characterized by the lower S content: $11.73 - 11.92$ apfu (Table 2), while its theoretical value is 12.00, and, in general, by the higher contents of $(As + Sb)$: $3.96 - 4.23$ apfu, with theoretical 4.00, whereas data published by Botinelly et al. (1973) and Chen and Szymański (1981) (Table 1, an. 3, $5 - 7$) show $12.26 - 12.53$ apfu S and $3.70 - 3.84$ apfu $(As + Sb)$. Obtained by us composition of a crystal from Getchell (Table 2, an. 2) fits within limits indicated by Chen and Szymański (1981, 1982) for their samples (Table 1, an. 8), for all constituents except As, the content of which is higher in our analysis. Taking into consideration that the above mentioned deviations from the ideal stoichiometry stable for samples from different deposits, including ones from Getchell studied independently by different researchers using different methods, it can be considered that observed differences are caused only by systematic errors caused by the chosen techniques and analytical conditions.

It is seen in Table 2 that the original galkhaite from Gal-Khaya deposit contains a large amount of cesium (5.8 wt.%), with strong prevailing of Cs over Tl i.e. it is identical in the ideal formula to the mineral from Khaidarkan, Getchell and Chauvay. Thus, it became clear that at the initial stage of the study of galkhaite from Gal-Khaya (Gruzdev et al., 1972; Kaplunnik et al., 1975) both cesium and its site in the structure were missed.

Galkhaite from Chauvay (Table 2, an. $5 - 7$) generally is also close in its composition to the mineral from other deposits. Galkhaite from the

Table 2. **Chemical composition of galkhaite: our electron microprobe data**

Constituents	1	2	3	4	5	6	7
				wt %			
Cs	5.78	6.61	3.62	4.47	5.78	6.00	6.27
Tl	0.77	0.97	0.20	2.82	0.32	0.43	0.49
Hg	52.88	50.57	52.24	51.84	52.00	51.91	51.16
Cu	3.37	3.49	3.25	2.84	1.76	1.97	3.52
Zn	0.58	1.23	1.80	0.99	0.86	1.07	1.24
Ag	н.п.о.	0.11	0.31	1.03	2.85	2.68	0.11
As	16.82	17.17	15.65	14.52	14.31	14.42	15.29
Sb	0.29	0.50	3.36	2.24	3.80	3.24	2.93
S	20.73	20.96	21.17	20.46	20.16	20.24	20.65
Total	101.22	101.61	101.60	101.21	101.84	101.96	101.66
	Formula calculated on (Hg + Cu + Zn + Ag + As + Sb + S) = 22						
Cs	0.80	0.90	0.48	0.63	0.81	0.84	0.86
Tl	0.07	0.09	0.02	0.26	0.03	0.04	0.04
Σ(Cs,Tl)	0.87	0.99	0.50	0.89	0.84	0.88	0.90
Hg	4.84	4.57	4.625	4.83	4.84	4.82	4.67
Cu	0.97	0.995	0.91	0.83	0.52	0.58	1.01
Zn	0.16	0.34	0.49	0.28	0.25	0.305	0.35
Ag	—	0.02	0.05	0.18	0.49	0.46	0.02
Σ(Hg,Cu,Zn,Ag)	5.97	5.925	6.075	6.12	6.10	6.165	6.05
As	4.12	4.15	3.71	3.62	3.57	3.585	3.73
Sb	0.045	0.075	0.49	0.34	0.58	0.495	0.44
Σ(As,Sb)	4.165	4.225	4.20	3.96	4.15	4.08	4.17
S	11.865	11.85	11.725	11.92	11.75	11.755	11.78

Notes: b.d.l. — below detection limit.
Contents of Na, K, Rb, Ca, Sr, Ba, Pb, Cd, Fe, Se, Te are b.d.l. in all specimens.
1 — sample #2046, Gal-Khaya; 2 — sample #2047, Getchell; 3 — sample #2048, Khaidarkan, Kara-Archa area;
4 — sample #2049, Khaidarkan; 5 — sample #2050, Chauvay; 6 — sample #2051, Chauvay; 7 — sample #2052,
Chauvay.

areas of the Chauvay deposit, where it is ore-forming mineral (samples #2050 and #2051), has a distinct feature — an unusually high Ag content — up to 2.9 wt.%. Our attempts to find any publications on the silver-bearing galkhaite have failed, except for a note about the presence of Ag among admixtures cited for this mineral in the reference book by Chvileva et al. (1988). Silver (1.0 wt.%) was also detected by us in the sample #2049 from Khaidarkan (table 2, an. 4). In this instance, this element probably occupies in galkhaite the same site as Hg, Cu and Zn.

Summarize the data seem reliable, both earlier published and newly obtained ones, it is possible to define the following, up-to-date proved, limits of variations for contents of the main chemical constituents in galkhaite (bold-type indicates species-forming elements), wt. %: Cs **3.3−7.1**, Tl 0.0−4.2, Hg 47.6−53.0, Cu 1.6−3.6, Zn 0.3−3.0, Fe 0.0−0.5, Ag 0.0−2.9, As **14.3−17.2**, Sb 0.0−5.5, S **20.2−22.7**.

All of our attempts to detect in galkhaite some other alkaline and alkaline-earth metals, besides Cs, and Pb in amounts above detection limits, have failed. Earlier, rubidium was detect-

ed in two samples of galkhaite from the Getchell mine: 220 and 257 ppm (Tretbar et al., 2000). Thus it is easy to calculate that the Rb/Cs atomic ratio in Getchell galkhaite is 0.005−0.01. According to our data, in samples from other occurrences the ratio does not exceed this level significantly, as well as values of K, Na, Ca, Sr, Ba, Pb ratios to Cs. This means that Tl really is the only element, which substitutes Cs in galkhaite in noticeable amounts, i.e. galkhaite should be called the selectively cesium mineral in the part of alkaline and alkaline-earth elements. A prevailing of Tl over Cs in atomic proportions has not been found in any known analyses of galkhaite.

Insignificant substitutions of Cs by other, except Tl, elements in galkhaite and an absence of any analogs, both natural and synthetic, of this mineral with other species-forming elements in the site inside the 12-fold polyhedron, is probably caused by the very large size of this polyhedron. For instance, the average <(Cs,Tl)-S> distance in galkhaite is 3.863 Å (Chen, Szymański, 1981), whereas in the synthetic analogue of pautovite, $CsFe_2S_3$, with rasvumite structure, the

average <Cs-S> distance in the 10-fold polyhedron is 3.680 Å (Mitchell *et al.*, 2004). The rasvumite structure type, AFe_2S_3, includes sulfides with A = K (rasvumite), Tl (picotpaulite), Cs (pautovite) and Rb (a synthetic phase), while substitutions in the A site are significant (Chakhmouradian *et al.*, 2001; Mitchell *et al.*, 2004; Pekov *et al.*, 2005), whereas in galkhaite the Cs atom, the largest one among above listed elements, is always and strongly dominating in the site inside the 12-fold polyhedron.

Data given in Tables 1 and 2 show that, with the above suggested way to calculate the formula, the (Cs + Tl) content varies from 0.50 to 1.02 *apfu*. The limits of these variations change weakly if other ways of calculation have been used: on the basis of S = 12, (S + As + Sb) = 16, etc. We supposed that the deficiency may be caused by presence of H_2O molecules and/or hydronium ions $(H_3O)^+$ together with Cs and Tl in the large 12-fold polyhedron, like in some oxygen-bearing minerals with large monovalent cations, namely micas, zeolites, margaritasite, members of the alunite and labuntsovite groups, etc. The infrared spectrum of galkhaite from Chauvay (sample #2050) obtained by N.V. Chukanov showed the absence of H-bearing groups. Chen and Szymański (1981) have noted that the (Cs,Tl) site in the studied crystal structure is vacant for 18.5%. Deficiency of (Cs + Tl) in our samples probably indicates that the 12-fold polyhedron is also partially vacant. According to both earlier-published and our data (Tables 1 and 2), the occupancy of the (Cs,Tl) site is 50 – 100%. Basing on this assumption, we suggest to refine the idealized formula of galkhaite from (Cs,Tl) $(Hg,Cu,Zn)_6(As,Sb)_4S_{12}$ (after Chen & Szymański, 1981) to $(Cs,Tl)_{0.5-1}(Hg,Cu,Zn)_6(As,Sb)_4S_{12}$.

Galkhaite is a very interesting mineral both from the viewpoints of geochemistry and genetic crystal chemistry. It is itself remarkable that a sulfide has become the most effective concentrator of cesium, the most typical lithophile element, and a single cesium mineral in the low-temperature hydrothermal ore deposits. Evidently, in the Getchell and Chauvay deposits, where this mineral is widespread, the Cs content in orebodies is higher than the average value for the Earth crust for many thousands times. The indicating geochemical role of galkhaite consists of the fact that, due to its specific "broad-porous" structure, it fixes the high-mobile cesium and appears as the main "witness" evidencing the high activity of cesium when these ore deposit were formed.

From the other side, the uniqueness of galkhaite, as the only representative of the structural type, and the presence of the species-forming cesium in it, are unambiguously demonstrate that the high concentration of this alkaline element in the mineral-forming media is necessary for appearance of this sulfosalt.

Presence of large cages, where cesium is located, in the galkhaite structure makes this mineral similar to zeolites and other microporous minerals. As it is known from theoretical crystal chemistry (Belov, 1976) and the practics of synthesis of crystals with zeolite-like structures (Barrer, 1985), the framework forms around large cations-modificators; for galkhaite, it is just cesium that emerges as the needed modificator.

Indeed, it seems that just concentration of cesium is the main factor determining the amount of galkhaite in the process of the arsenic-antimony-mercury ore formation and, consequently, quantitative relations of galkhaite with cinnabar, realgar and other coexisting sulfides of Hg and As. In this way, lest paradoxically it sounds, the cesium activity in a hydrothermal solution may control the type of mercury mineralization, including the commercially recoverable one.

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