

## CRYSTAL CHEMISTRY OF MERCURY SULFOSALTS – GALKHAITE, $(\text{Hg}_{5+x}\text{Cu}_{1-x})\text{Cs}_{1-x}\text{As}_4\text{S}_{12}$ ( $x \approx 0$ ): CRYSTAL STRUCTURE AND REVISION OF THE CHEMICAL FORMULA

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### ABSTRACT

Three specimens of galkhaite from the Getchell mine (G), Nevada, USA; the Gal-Khaya As-Hg-Sb deposit (Gk), Yakutia, Russia; and Signols (S), Piedmont, Italy, have been fully characterized through single-crystal X-ray diffraction and electron-microprobe analyses. Chemical data indicate the formulae  $[(\text{Hg}_{4.61}\text{Zn}_{0.38}\text{Fe}_{0.04})_{\Sigma 5.03}(\text{Cu}_{0.03}\text{Ag}_{0.04})_{\Sigma 1.07}]\text{Cs}_{6.10}\text{Ti}_{0.20}\text{S}_{12.06}$  (G),  $[(\text{Hg}_{4.66}\text{Zn}_{0.32})_{\Sigma 4.98}(\text{Cu}_{0.55}\text{Ag}_{0.45})_{\Sigma 1.00}]\text{Cs}_{0.74}\text{Ti}_{0.06}\text{S}_{12.05}$  (Gk), and  $[(\text{Hg}_{4.10}\text{Zn}_{0.85})_{\Sigma 4.95}(\text{Cu}_{0.89}\text{Ag}_{0.16})_{\Sigma 1.05}]\text{Cs}_{0.95}(\text{As}_{3.64}\text{Sb}_{0.16})_{\Sigma 3.80}\text{S}_{12.19}$  (S). Unit-cell parameters are  $a = 10.405(3)$  Å (G),  $10.443(1)$  Å (Gk), and  $10.332(2)$  Å (S), space group  $\bar{I}\bar{4}3m$ . The crystal structure of the three specimens has been solved to  $R_1 = 0.029$  (G),  $0.028$  (Gk), and  $0.031$  (S). It is a three-dimensional framework of  $\text{HgS}_4$  and  $\text{As}_3\text{S}_4$  polyhedra, with Cs hosted in large 12-fold coordinated cavities. The introduction of  $\text{Cs}^+$ , as well as minor  $\text{Ti}^+$ , at these structural positions requires the replacement of  $\text{Hg}^{2+}$  by  $\text{Cu}^+$ . The mixed site occupancy at the Hg site of galkhaite is a case of valency-imposed double site-occupancy. Consequently, the idealized chemical formula of galkhaite can be written as  $(\text{Hg}_5\text{Cu})\text{CsAs}_4\text{S}_{12}$ . Taking into account the possible existence of vacancy in the structural cavities, the formula can be generalized as  $(\text{Hg}_{5+x}\text{Cu}_{1-x})\text{Cs}_{6}\text{As}_{1-x}\text{S}_{12}$  ( $x \approx 0$ ).

**Keywords:** galkhaite, crystal-chemistry, sulfosalt, cesium, mercury, copper, arsenic.

### INTRODUCTION

Galkhaite is the only cesium sulfosalt mineral known to date and is related to the tetrahedrite isotypic series (Moëlo *et al.* 2008). It was first described by Gruzdev *et al.* (1972) from the Gal-Khaya deposit, Yakutia, Russia, and the Khaidarkan deposit, Kyrgyzstan, with the chemical formula  $\text{HgAsS}_2$ . Then Divjaković & Nowacki (1975) solved its crystal structure using a crystal from the Getchell mine, Nevada, USA, and detected the presence of a site occupied by a heavy element in 12-fold coordination; using the chemical data reported by Botinelly *et al.* (1973), they concluded that this site was occupied by thallium, with a site occupancy of a bit less than half. Another structural model was proposed by Kaplunnik *et al.* (1975), with a worse  $R$  factor, placing a combination

of  $\text{As}^{3-}$  and  $\text{As}_4$  groups into the cavities. Finally, Chen & Szymański (1981, 1982) proved that Cs generally exceeds Tl in galkhaite and proposed the crystal-chemical formula  $(\text{Cs}, \text{Tl}, \square)(\text{Hg}, \text{Cu}, \text{Zn}, \text{Ti})_6(\text{As}, \text{Sb})_4\text{S}_{12}$ ; according to these authors, Tl partially replaces Cs at the 12-fold coordinated site and may occur in minor amount also in tetrahedral coordination as  $\text{Ti}^{3+}$ . These authors explained the structural model of Kaplunnik *et al.* (1975) as an attempt to fit the structure to the chemistry given by Gruzdev *et al.* (1972). Finally, chemical data for galkhaite from its type locality Gal-Khaya and from the Chauvay mine, Kyrgyzstan, have been reported by Vasil'ev *et al.* (2010), confirming the Cs-rich nature of this mineral; moreover, these authors gave structural data for the specimen from the Chauvay mine. A review of the history of studies of galkhaite is given by Pekov & Bryzgalov (2006).

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The crystal structure of galkhaite can be described as a three-dimensional tetrahedrite-like framework, with  $(\text{Hg,Cu,Zn,Ag,Fe})\text{S}_4$  tetrahedra and  $(\text{As,Sb})\text{S}_3$  trigonal pyramids. Large cavities host cesium in 12-fold coordination; the coordination polyhedron can be described as a Laves polyhedron, *i.e.*, a truncated tetrahedron. The chemical variability of galkhaite is related to the occupancies at the 12-fold coordinated and at the tetrahedral sites. Chen & Szymański (1981) reported a negative correlation between Cs and Tl and the existence of zoned crystals with a Cs-rich periphery and a Tl-rich core. The latter showed  $\text{Tl} > \text{Cs}$ , corresponding to a potential new chemical pole, the Tl-analogue of galkhaite. In addition, the specimen from Khaidarkan studied by Chen & Szymański (1982) showed a low ( $\text{Cs} + \text{Tl}$ ) total, confirmed later by Pekov & Bryzgalov (2006) for a specimen from the Kara-Archa area in the Khaidarkan ore district. These latter authors proposed the idealized chemical formula  $(\text{Cs,Tl})_{0.5-1}(\text{Hg,Cu,Zn})_6(\text{As,Sb})_4\text{S}_{12}$  for galkhaite.

New single-crystal X-ray diffraction and electron-microprobe data were collected from three specimens of galkhaite from different occurrences, aiming at clarifying some aspects of the crystal chemistry of galkhaite, and in particular the relationships between the site occupancies at the 12-fold coordinated and the tetrahedral sites.

## EXPERIMENTAL

Three specimens from different occurrences were studied. A brief description of each follows: (i) Galkhaite from the Getchell mine, Nevada, USA. Well-shaped red cubic crystals, up to 3 mm, with quartz. (ii) Galkhaite from the Gal-Khaya As-Hg-Sb deposit, Yakutia, Eastern-Siberian Region, Russia. Orange-red veinlets in a black schist. Specimen # 2980/I in the mineralogical collection of the Museo di Storia Naturale, University of Florence, Italy. (iii) Galkhaite from Signols, Piedmont, Italy. Anhedral orange grain (~0.5 mm in size), strictly associated with sulfur and orpiment, from Upper Triassic evaporites. Specimen # 19381 in the mineralogical collection of the Museo di Storia Naturale, University of Pisa, Italy. It is the same specimen briefly described by Biagioli *et al.* (2010).

## Crystallography

For the X-ray single-crystal studies, the intensity data were collected using a Bruker Smart Breeze diffractometer with an air-cooled CCD detector, with graphite-monochromatized  $\text{MoK}\alpha$  radiation. The detector-to-crystal working distance was 50 mm. Details of data collections and crystal structure refinements are given in Table 1. Data were corrected for Lorentz, polarization, and absorption factors using the software package Apex2 (Bruker AXS Inc. 2004).

The crystal structures of galkhaite from the three occurrences were refined starting from the atomic coordinates given by Chen & Szymański (1981) using SHELXL-97 (Sheldrick 2008). Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson 1992).

Three independent cation sites, labelled as Cs, Hg, and As, and one S site occur in the crystal structure of galkhaite. The occupancies of the three independent cation sites were refined using the following scattering curves: Cs site, Cs *versus*  $\square$ ; Hg site, Hg *versus* Cu; As site, As *versus* Sb. After several cycles of refinement, the final  $R_1$  converged to 0.029, 0.028, and 0.031 for the crystals of galkhaite from the Getchell mine, the Gal-Khaya As-Hg-Sb deposit, and Signols, respectively. Atomic coordinates and displacement parameters are given in Table 2; selected bond distances are given in Table 3.

## Electron-microprobe data

The crystals used for the single-crystal X-ray diffraction study were embedded in epoxy and quantitatively analyzed by electron microprobe using a Superprobe Jeol JXA 8200 installed at the "Eugen F. Stumpfl Laboratory" at the University of Leoben (Austria), operating in WDS mode. The quantitative analyses were obtained using 20 kV accelerating voltage and 10 nA beam current. The counting time for peak and both backgrounds (left and right) were 20 and 10 seconds, respectively. The beam diameter was about 1  $\mu\text{m}$ . The position of the measurement of backgrounds was carefully selected to avoid overlapping among the analyzed elements. The grains were analyzed using  $\text{PtAs}_2$ ,  $\text{CuSe}$ ,  $\text{AgBiSe}_2$ ,  $\text{Ti}(\text{Br,I})$  for As, Se, Ag, and Tl, and natural stibnite, cinnabar, pollucite, chalcopyrite, and sphalerite for As, S, Sb, Hg, Cs, Cu, Zn, and Fe. The X-ray lines used were:  $K\alpha$  for S, Fe, Zn, and Cu;  $L\alpha$  for As, Se, Sb, Ag, and Cs;  $M\alpha$  for Hg and Tl. The following diffracting crystals were selected: TAP for As and Se; PETJ for S, Sb, and Ag; PETH for Hg, Tl and Cs; LIFH for Cu, Zn and Fe. The detection limits (ppm) for the analyzed elements, automatically calculated by the microprobe software, were as follows: As = 270, Se = 440, S = 130, Sb = 370, Ag = 340, Hg = 350, Tl = 600, Cs = 190, Cu = 260, Zn = 170, and Fe = 290. Back scattered electron (BSE) images, obtained using the same instrument, showed the homogeneity of the studied grains. The results of the chemical analyses are given in Table 4. The low analytical totals for the grains from Gal-Khaya and Signols is probably due to the poor quality of the polished surfaces and, for the latter, to its very small size.

Following Pekov & Bryzgalov (2006), the crystal-chemical formulae were recalculated on the basis of  $\Sigma(\text{Me} + \text{S}) = 22$  atoms per formula unit (*apfu*), with Me = tetrahedral cations and pnictogens. The three

TABLE 1. DETAILS OF THE DATA COLLECTIONS AND CRYSTAL STRUCTURE REFINEMENTS

Crystal data	Getchell	Gal-Khaya	Signols
Crystal size (mm)	$0.05 \times 0.04 \times 0.04$	$0.20 \times 0.15 \times 0.10$	$0.06 \times 0.05 \times 0.04$
Cell setting, space group		Cubic, $I\bar{4}3m$	
$a$ (Å)	10.405(3)	10.443(1)	10.332(2)
$V$ (Å <sup>3</sup> )	1126.5(6)	1138.9(2)	1102.9(4)
$Z$	2	2	2
<b>Data collection and refinement</b>			
Radiation, wavelength (Å)		Mo $K\alpha$ , $\lambda = 0.71073$	
Temperature (K)		298	
Scan mode	$\omega$ and $\varphi$	$\omega$	$\omega$ and $\varphi$
Number of frames	682	448	537
Rotation width (°)	0.5	0.5	0.5
Exposure time (s)	25	7	25
Maximum observed $2\theta$ (°)	52.54	65.02	64.99
Measured reflections	2162	2570	2174
Unique reflections	237	372	382
Reflections $F_o > 4\sigma(F_o)$	208	354	296
$R_{int}$ after absorption correction	0.0389	0.0449	0.0438
$R\sigma$	0.0265	0.0364	0.0417
Range of $h$ , $k$ , $l$	$-11 \leq h \leq 11$ , $-11 \leq k \leq 12$ , $-12 \leq l \leq 12$	$-9 \leq h \leq 15$ , $-14 \leq k \leq 12$ , $-15 \leq l \leq 13$	$-9 \leq h \leq 13$ , $-7 \leq k \leq 15$ , $-8 \leq l \leq 14$
$R$ [ $F_o > 4\sigma F_o$ ]	0.0294	0.0281	0.0314
$R$ (all data)	0.0408	0.0296	0.0522
$wR$ (on $F_o^2$ )	0.0577	0.0686	0.0608
GooF	1.150	1.119	1.186
Number of least-squares parameters	17	17	17
Maximum and minimum residual peak (e/Å <sup>3</sup> )	1.82 (at 1.06 Å from Cs) -2.49 (at 0.53 Å from Cs)	1.15 (at 0.94 Å from Cs) -1.48 (at 0.41 Å from Cs)	1.07 (at 1.85 Å from Cs) -1.21 (at 1.79 Å from S)

samples have the following compositions: (1) ( $Hg_{4.61(5)}Zn_{0.38(2)}Fe_{0.04(4)}Cu_{1.03(2)}Ag_{0.04(2)}\Sigma 6.10(Cs_{0.76(6)}Tl_{0.20(8)})\Sigma 0.96(As_{3.81(4)}Sb_{0.04(3)})\Sigma 3.85S_{12.06(6)}$ ) (Getchell mine), (2) ( $Hg_{4.66(4)}Zn_{0.32(1)}Cu_{0.55(3)}Ag_{0.45(2)}\Sigma 5.98(Cs_{0.74(2)}Tl_{0.06(1)})\Sigma 0.80(As_{3.42(11)}Sb_{0.56(5)})\Sigma 3.98S_{12.05(7)}$ ) (Gal-Khaya As-Hg-Sb deposit), and (3) ( $Hg_{4.10(4)}Zn_{0.85(23)}Cu_{0.89(1)}Ag_{0.16(1)}\Sigma 6.00Cs_{0.95(2)}(As_{3.64(3)}Sb_{0.16(1)})\Sigma 3.80S_{12.19(4)}$ ) (Signols).

The cation ratios can be considered satisfying. The sum of tetrahedral cations ranges between 5.98 and 6.10  $apfu$ , in good agreement with the ideal 6  $apfu$ . The sum (Cs + Tl) approaches 1  $apfu$ , with a larger deficit in the specimen from Gal-Khaya. The hypothesis of a partial replacement of these two cations by  $Na^+$ ,  $K^+$ ,  $Rb^+$ , or  $Ba^{2+}$  was checked through qualitative WDS analyses that showed the absence of these elements. Finally, the total (As + Sb) sum is generally below the ideal value of 4  $apfu$ , ranging between 3.80 and 3.98  $apfu$ .

The valence equilibrium value  $Ev$  (%), defined as  $[\Sigma(\text{val}+) - \Sigma(\text{val}-)] \times 100/\Sigma(\text{val}-)$ , is slightly negative, owing to the pnictogen deficit and the S excess. The (As + Sb) deficit has been observed in other

compositions from literature, e.g., for specimens from the Getchell mine (Chen & Szymański 1981), with an average (As + Sb) content of 3.70  $apfu$ . On the contrary, the analyses reported by Pekov & Bryzgalov (2006) and Vasil'ev *et al.* (2010) show an (As + Sb) excess, up to 4.23  $apfu$ . This could indicate some analytical problem, such as the lack of suitable standards that would confidently duplicate the galkhaite matrix, as suggested by Chen & Szymański (1981). Taking into account the three specimens studied in the present work, the (As + Sb) deficit of the samples from the Getchell mine and Signols is not confirmed by the structural refinements that point to a full occupancy of the As site (see below). Consequently, the deficit may be an analytical artifact. The S excess in the samples from the Getchell mine and Gal-Khaya can be neglected, being within the standard deviation. On the contrary, a larger S excess (and a consequently more negative  $Ev$  value) was measured for the sample from Signols; indeed, it could be related to the quality of this analysis as described above.

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR GALKHAITE

	s.o.f.	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{\text{eq}}$
<b>Getchell</b>	Hg	$\text{Hg}_{0.82}\text{Cu}_{0.18}$	$\frac{1}{4}$	$\frac{1}{2}$	0	$0.0643(8)$	$0.0262(4)$	0	0	0	$0.0389(4)$
	Cs	$\text{Cs}_{0.99}$	0	0	0	$0.071(2)$	$0.071(2)$	0	0	0	$0.071(2)$
	As	$\text{As}_{0.94}\text{Sb}_{0.06}$	$0.2458(3)$	$0.2458(3)$	$0.2458(3)$	$0.0203(8)$	$0.0203(8)$	$-0.0025(5)$	$-0.0025(5)$	$-0.0025(5)$	$0.0203(8)$
	S	$\text{S}_{1.00}$	$0.3882(3)$	$0.3882(3)$	$0.1626(4)$	$0.026(2)$	$0.026(2)$	$0.0008(11)$	$0.0008(11)$	$-0.009(2)$	$0.024(2)$
<b>Gal-Khaya</b>	Hg	$\text{Hg}_{0.84}\text{Cu}_{0.16}$	$\frac{1}{4}$	$\frac{1}{2}$	0	$0.0540(4)$	$0.0243(2)$	$0.0243(2)$	0	0	$0.0342(2)$
	Cs	$\text{Cs}_{0.92}$	0	0	0	$0.0498(10)$	$0.0498(10)$	$0.0498(10)$	0	0	$0.0498(10)$
	As	$\text{As}_{0.81}\text{Sb}_{0.19}$	$0.2448(1)$	$0.2448(1)$	$0.2448(1)$	$0.0185(4)$	$0.0185(4)$	$0.0185(4)$	$-0.0003(3)$	$-0.0003(3)$	$0.0185(4)$
	S	$\text{S}_{1.00}$	$0.3884(2)$	$0.3884(2)$	$0.1632(2)$	$0.0223(9)$	$0.0223(9)$	$0.0199(13)$	$0.0019(6)$	$-0.0064(9)$	$0.0215(8)$
<b>Signols</b>	Hg	$\text{Hg}_{0.64}\text{Cu}_{0.36}$	$\frac{1}{4}$	$\frac{1}{2}$	0	$0.0552(6)$	$0.0228(3)$	$0.0228(3)$	0	0	$0.0336(3)$
	Cs	$\text{Cs}_{1.01}$	0	0	0	$0.0425(8)$	$0.0425(8)$	$0.0425(8)$	0	0	$0.0425(8)$
	As	$\text{As}_{0.93}\text{Sb}_{0.07}$	$0.2439(2)$	$0.2439(2)$	$0.2439(2)$	$0.0197(5)$	$0.0197(5)$	$0.0197(5)$	$-0.0024(4)$	$-0.0024(4)$	$0.0197(5)$
	S	$\text{S}_{1.00}$	$0.3876(2)$	$0.3876(2)$	$0.1604(3)$	$0.0264(12)$	$0.0264(12)$	$0.0259(18)$	$0.0014(8)$	$-0.0014(8)$	$-0.0091(12)$

TABLE 3. SELECTED BOND DISTANCES (IN  $\text{\AA}$ ) IN GALKHAITE

	Getchell	Gal-Khaya	Signols
Hg–S	$2.507(3) \times 4$	$2.521(2) \times 4$	$2.473(2) \times 4$
Cs–S	$3.877(4) \times 12$	$3.884(3) \times 12$	$3.874(3) \times 12$
As–S	$2.267(4) \times 3$	$2.286(2) \times 3$	$2.270(3) \times 3$

## CRYSTAL STRUCTURE DESCRIPTION

## General organization

Galkhaite belongs to a series of compounds having a sphalerite-like structure (e.g., Borisov *et al.* 2009).  $\text{HgS}_4$  tetrahedra form a three-dimensional framework through corner-sharing. Arsenic trigonal pyramids are located in trigonal cavities along the triad axis in the Hg framework, being bonded to Hg tetrahedra through corner-sharing. Finally, Cs, as well as minor Tl, are hosted within large 12-fold coordinated cavities.

## Cation coordination and site occupancies

As reported above, three independent cation sites occur in the crystal structure of galkhaite.

The Hg site has a regular tetrahedral coordination, with bond distances of  $2.473(2)$ ,  $2.507(3)$ , and  $2.524(2)$   $\text{\AA}$  for the specimens from Signols, Getchell mine, and Gal-Khaya, respectively. The bond length of the Hg site of the specimen from the Getchell mine compares well with the data given by Chen & Szymański (1981), *i.e.*,  $2.496(1)$   $\text{\AA}$ . Such a variation between the three samples is related to the chemical variability of the Hg site. Indeed, it is a site with a mixed (Hg, Zn, Cu, Ag, Fe) site occupancy, as confirmed by the comparison between the site scattering values and the proposed site populations given in Table 5. Similar sites with a mixed occupancy have been reported in other Hg sulfosalts, *e.g.*, arsiccoite (Biagioni *et al.* 2014b).

The As site forms a trigonal pyramid with three S atoms, with average bond distance ranging from  $2.267(4)$  to  $2.289(2)$   $\text{\AA}$  for the specimens from the Getchell mine and Gal-Khaya, respectively. The variation in the average bond length is related to the minor Sb content.

The 12-fold coordinated Cs site has been described as a Laves polyhedron. The three S determining the four triangular faces are bonded to the As site. The three specimens show only negligible variations in the  $\langle \text{Cs–S} \rangle$  bond distance, notwithstanding the partial replacement of  $\text{Cs}^+$  by the smaller  $\text{Tl}^+$  cations in the specimens from Getchell and Gal-Khaya and the pure  $\text{Cs}^+$  nature of the Italian galkhaite. Makovicky (2005) pointed out that the equivalent isotropic displacement parameter of Cs, larger than that of

TABLE 4. MICROPROBE ANALYSES OF GALKHAITE

Element	Getchell ( <i>n</i> = 32)			Gal-Khaya ( <i>n</i> = 11)			Signols ( <i>n</i> = 2)	
	wt.%	range	e.s.d.	wt.%	range	e.s.d.	wt.%	e.s.d.
Cu	3.54	3.41–3.72	0.09	1.82	1.67–1.98	0.10	3.15	0.05
Ag	0.22	0.02–0.36	0.08	2.55	2.38–2.82	0.14	0.98	0.02
Zn	1.35	1.15–1.49	0.08	1.11	1.02–1.17	0.04	3.09	0.92
Fe	0.11	0.00–0.41	0.12	0.01	0.00–0.05	0.02	0.01	0.01
Hg	50.23	49.58–50.92	0.38	49.12	48.54–49.89	0.43	45.48	3.21
Cs	5.51	4.67–6.16	0.44	5.17	5.07–5.29	0.07	6.97	0.09
Tl	2.19	0.71–3.66	0.91	0.60	0.50–0.65	0.04	n.d.	
As	15.51	15.14–15.94	0.20	13.47	12.49–14.16	0.47	15.14	1.39
Sb	0.25	0.00–0.90	0.17	3.57	2.96–3.83	0.33	1.11	0.06
S	21.01	20.44–21.32	0.21	20.32	19.95–20.50	0.17	21.68	0.56
Se	0.00	0.00–0.04	0.01	0.00	0.00–0.01	0.00	n.d.	
Total	99.92	98.71–101.18	0.48	97.74	96.85–98.61	0.53	97.60	0.15
	<i>apfu</i>	range	e.s.d.	<i>apfu</i>	range	e.s.d.	<i>apfu</i>	e.s.d.
Cu	1.026	0.986–1.067	0.021	0.546	0.495–0.590	0.031	0.894	0.012
Ag	0.037	0.004–0.062	0.014	0.450	0.417–0.494	0.025	0.163	0.007
Zn	0.381	0.321–0.422	0.024	0.322	0.296–0.338	0.012	0.848	0.230
Fe	0.037	0.000–0.133	0.038	0.004	0.000–0.018	0.007	0.003	0.003
Hg	4.609	4.510–4.708	0.051	4.656	4.617–4.740	0.039	0.946	0.015
Cs	0.764	0.651–0.846	0.057	0.740	0.727–0.758	0.011	4.095	0.407
Tl	0.197	0.063–0.332	0.083	0.056	0.046–0.060	0.004	n.d.	
As	3.811	3.744–3.945	0.044	3.417	3.176–3.586	0.113	3.640	0.229
Sb	0.037	0.000–0.134	0.026	0.557	0.461–0.601	0.052	0.164	0.005
S	12.062	11.879–12.149	0.061	12.048	11.944–12.180	0.071	12.193	0.035
Se	0.000	0.000–0.009	0.002	0.000	0.000–0.002	0.001	n.d.	
Cs+Tl	0.961	0.910–1.014	0.029	0.796	0.779–0.814	0.011	0.946	0.015
Hg+Zn+Fe	5.027	4.962–5.090	0.029	4.982	4.941–5.065	0.038	4.942	0.177
Cu+Ag	1.063	1.028–1.100	0.015	0.996	0.976–1.035	0.016	1.058	0.019
As+Sb	3.848	3.764–3.965	0.047	3.974	3.754–4.099	0.093	3.804	0.234
Ev	-2.1	-3.6–1.6	1.2	-1.7	-4.7–0.6	1.5	-4.4	1.5

Chemical composition as wt.% and number of atoms on the basis of  $\Sigma(Me + S) = 22$  *apfu* (with Me = tetrahedral cations and pnictogens). Valence equilibrium:  $Ev (\%) = [\Sigma(\text{val}+) - \Sigma(\text{val}-)] \times 100 / \Sigma(\text{val}-)$ .

S in the framework, suggests large movements (" rattling") of (Cs,Tl) in the cavity. The three structural refinements reported in this work agrees with Makovicky's statement.

#### CRYSTAL CHEMISTRY

##### Structural formula

The X-ray formulae of galkhaite from the three different occurrences are: (1)  $(Hg_{4.92}Cu_{1.08})Cs_{0.99}(As_{3.76}Sb_{0.24})S_{12}$  (Getchell mine); (2)  $(Hg_{5.04}Cu_{0.96})Cs_{0.92}(As_{3.24}Sb_{0.76})S_{12}$  (Gal-Khaya); and (3)  $(Hg_{3.84}Cu_{2.16})Cs_{1.01}(As_{3.72}Sb_{0.28})S_{12}$  (Signols).

Whereas formulae (1) and (2) have *Ev* values close to 0 (-0.38 and -0.17%, respectively), the X-ray formula of galkhaite from Signols has a relative error of the valence equilibrium  $Ev = -4.8\%$ . This

negative error is related to the occurrence of a significant amount of Zn replacing Hg, thus lowering the site scattering at the Hg site. Taking into account the site scattering values and the electron-microprobe data, the site populations given in Table 5 can be proposed. Thus, the three specimens have the following idealized chemical formulae: (1)  $[(Hg_{4.56}Zn_{0.36})S_{12}(Cu_{1.02}Ag_{0.06})S_{12}]$  (Getchell mine); (2)  $[(Hg_{4.68}Zn_{0.30})S_{12}(Cu_{0.54}Ag_{0.48})S_{12}]$  (Gal-Khaya); and (3)  $[(Hg_{4.08}Zn_{0.84})S_{12}(Cu_{0.90}Ag_{0.18})S_{12}]$  (Signols). These formulae can be simplified as  $[(Hg, Zn)_5(Cu, Ag)]CsAs_4S_{12}$ .

##### Chemical variability in galkhaite

The study of the three specimens of galkhaite and examination of chemical data from the literature

TABLE 5. COMPARISON BETWEEN SITE SCATTERING VALUES (XRD), CALCULATED SITE SCATTERING ON THE BASIS OF ELECTRON-MICROPROBE DATA (EPMA), PROPOSED SITE POPULATION, AND COMPARISON BETWEEN CALCULATED AND OBSERVED AVERAGE BOND DISTANCES AT Hg, Cs, AND As SITES IN GALKHAITE

<b>Getchell</b>						
Site	XRD	EPMA	Site population	$\langle Me-S \rangle_{obs}$	$\langle Me-S \rangle_{calc}$	BVS
Hg	70.8	68.0	Hg <sub>0.76</sub> Cu <sub>0.17</sub> Zn <sub>0.06</sub> Ag <sub>0.01</sub>	2.507	2.528	2.05 (1.82)
Cs	54.4	60.5	Cs <sub>0.79</sub> Tl <sub>0.21</sub>	3.877	3.754	0.74 (1.00)
As	34.1	33.2	As <sub>0.99</sub> Sb <sub>0.01</sub>	2.267	2.262	2.96 (3.00)
<b>Gal-Khaya</b>						
Site	XRD	EPMA	Site population	$\langle Me-S \rangle_{obs}$	$\langle Me-S \rangle_{calc}$	BVS
Hg	71.8	70.3	Hg <sub>0.78</sub> Cu <sub>0.09</sub> Ag <sub>0.08</sub> Zn <sub>0.05</sub>	2.524	2.553	2.07 (1.83)
Cs	50.6	45.6	Cs <sub>0.74</sub> Tl <sub>0.06</sub> $\square$ <sub>0.20</sub>	3.888	-*	0.62 (0.80)
As	36.4	35.5	As <sub>0.86</sub> Sb <sub>0.14</sub>	2.289	2.287	3.03 (3.00)
<b>Signols</b>						
Site	XRD	EPMA	Site population	$\langle Me-S \rangle_{obs}$	$\langle Me-S \rangle_{calc}$	BVS
Hg	61.6	64.4	Hg <sub>0.68</sub> Cu <sub>0.15</sub> Zn <sub>0.14</sub> Ag <sub>0.03</sub>	2.473	2.516	2.16 (1.82)
Cs	55.6	55.0	Cs <sub>1.00</sub>	3.874	3.809	0.84 (1.00)
As	34.3	34.1	As <sub>0.96</sub> Sb <sub>0.04</sub>	2.270	2.268	3.00 (3.00)

Bond valence sums (BVS) are calculated according to the parameters given by Brese & O'Keeffe (1991). In mixed sites, bond-valence contribution of each cation has been weighted according to its occupancy. The calculated value is compared with the expected one (within parentheses). BVSs for S anion in the three samples are (in valence unit): 2.07 (Getchell), 2.10 (Gal-Khaya), and 2.15 (Signols).

Note: \* average  $\langle Me-S \rangle$  not given owing to the presence of vacancy.

(Chen & Szymański 1981, 1982, Pekov & Bryzgalov 2006, Vasil'ev *et al.* 2010) allow us to discuss the chemical variability of this mineral.

Among the specimens examined during this study, galkhaite from the Getchell mine is close to the 'ideal' galkhaite, with Hg partially replaced by Zn and Cs partially substituted by Tl. The other two samples show some chemical peculiarities. In particular, galkhaite from Signols is exceptionally enriched in Zn. It is the sample with the lowest Hg/(Hg+Zn) atomic ratio so far reported. And galkhaite from Gal-Khaya has a high Ag content, among the highest ever recorded and similar to those reported for galkhaite from Chauvay Sb-Hg deposit, Kyrgyzstan, with a Cu/(Cu + Ag) atomic ratio close to 0.50.

These chemical peculiarities are related to the site occupancy of the mixed tetrahedral Hg site hosting divalent and monovalent cations, *i.e.*, (Hg, Zn, Fe) and (Cu, Ag), respectively (Fig. 1). The homovalent substitution  $Hg^{2+} \rightarrow Zn^{2+}$  has been observed in other sulfosalts, such as the pair routhierite-stalderite,  $CuHg_2TlAs_2S_6$  and  $CuZn_2TlAs_2S_6$ , respectively, or in the pair aktashite-nowackiite,  $Cu_6Hg_3As_4S_{12}$  and  $Cu_6Zn_3As_4S_{12}$ , respectively (Moëlo *et al.* 2008). Among sulfides, the isotyprism between sphalerite, ZnS, and metacinnabar, HgS, is well known. Mixed (Hg,Cu) sites have been reported in few other natural sulfosalts and

have been reviewed by Biagioni *et al.* (2014c). Mercury can also be replaced by minor Fe, assumed to be  $Fe^{2+}$  in agreement with Makovicky *et al.* (1990); these authors suggested that the presence of Zn and Hg favors  $Fe^{2+}$  over  $Fe^{3+}$ . This kind of substitution has a negligible importance in galkhaite but has been observed by Graeser *et al.* (1995) in stalderite and by Bindi *et al.* (2012) in a new fettelite-like mineral. The heterovalent substitution  $Hg^{2+} \rightarrow Cu^+$  gives rise to a deficit of charges and consequently another substitution must occur. For example, Biagioni *et al.* (2014a) reported a cross-substitution between the two Hg and Cu<sub>2</sub> tetrahedral sites in the crystal structure of aktashite, with  $Hg^{2+}$  being partially replaced by  $Cu^+$  at the Hg site and  $Cu^+$  replaced by  $Hg^{2+}$  at the Cu<sub>2</sub> site. Additionally, the  $Hg^{2+} \rightarrow Cu^+$  substitution has been reported by Bindi *et al.* (2012) at the linearly coordinated Hg site of fettelite; also in this case, in order to maintain the electrostatic balance, some  $Ag^+$  is substituted by a divalent cation (*e.g.*,  $Zn^{2+}$ ).

In galkhaite, if the three-dimensional framework is taken into account, considering the tetrahedral sites fully occupied by Hg, the electrostatically neutral formula  $Hg_6As_4S_{12}$  is obtained. The introduction of Cs, as well as Tl, in the structural cavities of galkhaite is possible through the coupled substitution  $Hg^{2+} + \square = Cu^+ + (Cs, Tl)^+$ . Consequently, the site occupancy of

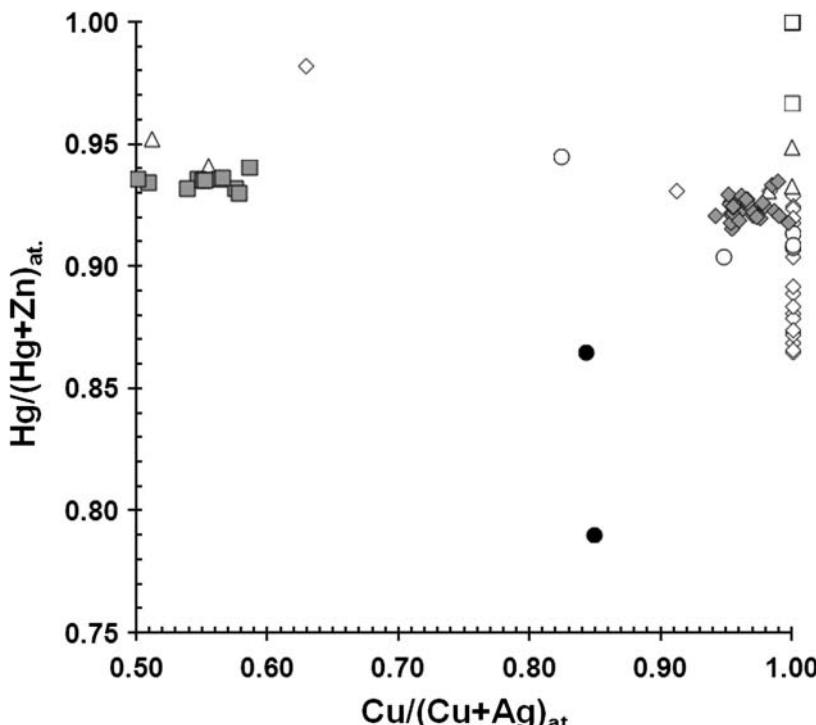


Fig. 1. Chemical variability of the occupancy of the tetrahedral site of galkhaite, expressed as a function of the atomic ratios  $\text{Cu}/(\text{Cu} + \text{Ag})$  versus  $\text{Hg}/(\text{Hg} + \text{Zn})$ . Symbols: rhombs: Getchell mine (literature data = grey; this work = white); square: Gal-Khaya (literature data = white; this work = grey); white circles = Khaidarkan; black circles = Signols; white triangles = Chauvay. Literature data after Chen & Szymański (1981, 1982), Pekov & Bryzgalov (2006), and Vasil'ev *et al.* (2010).

the mixed Hg site, related to the heterovalent substitution  $\text{Hg}^{2+} \rightarrow \text{Cu}^+$ , is a case of valency-imposed double site-occupancy (Hatert & Burke 2008). Therefore, the idealized chemical formula of galkhaite should be correctly written as  $(\text{Hg}_5\text{Cu})\text{CsAs}_4\text{S}_{12}$ , and not  $(\text{Cs}, \text{Ti}, \square)(\text{Hg}, \text{Cu}, \text{Zn}, \text{Ti})_6(\text{As}, \text{Sb})_4\text{S}_{12}$ , as reported in the official IMA list of Minerals (updated July 2014). Such valency-imposed double site-occupancy has been used in the classification of other sulfosalts (*e.g.*, carducciite; Biagioni *et al.*, in press) or in the tunnel oxides of the hollandite supergroup (Biagioni *et al.* 2013). Figure 2 shows the average  $(\text{Hg} + \text{Zn} + \text{Fe})$  and  $(\text{Cu} + \text{Ag})$  contents in galkhaite from different occurrences, confirming the 5:1 atomic ratio between divalent and monovalent cations. Copper plays the role of charge-compensating cation in galkhaite. As shown by the specimen from Gal-Khaya (as well as galkhaite from Chauvay studied by Pekov & Bryzgalov 2006),  $\text{Ag}^+$  can substitute for  $\text{Cu}^+$ . This kind of substitution is known in other compounds, *e.g.*, the tetrahedrite isotypic series or the pair routhierite-arsiccoite,  $\text{CuHg}_2\text{TLAs}_2\text{S}_6$  and  $\text{AgHg}_2\text{TLAs}_2\text{S}_6$ , respectively. Consequently, a possible Ag

endmember,  $(\text{Hg}_5\text{Ag})\text{CsAs}_4\text{S}_{12}$ , may be found in nature. Mixed  $(\text{Hg}, \text{Ag})$  sites have been observed in other sulfosalts, *e.g.*, rouxelite (Orlandi *et al.* 2005, Biagioni *et al.* 2014c).

The site occupancy of the tetrahedral site is closely related to the sum of cations occurring at the 12-fold coordinated sites. Notwithstanding the possible existence of vacancies, as suggested by the chemical analysis of galkhaite from Khaidarkan reported by Chen & Szymański (1982) and Pekov & Bryzgalov (2006), *i.e.*, 0.5  $(\text{Cs} + \text{Ti})$  *apfu*, the average  $(\text{Cs} + \text{Ti})$  content calculated from literature data is 0.89(4) *apfu*, consequently approaching the full site occupancy. In this respect, the  $(\text{Cs} + \text{Ti})$  deficit observed in the specimen from Gal-Khaya examined during this study could be an analytical artifact due to the bad quality of the polished surface or it can be due to the occurrence of minor amounts of an undetected component, *e.g.*, an  $\text{NH}_4^+$  group. The occurrence of minor amounts of  $\text{NH}_4^+$  in sulfosalts has been reported hypothetically by Zelenski *et al.* (2009) in tazieffite and was experimentally confirmed by Biagioni *et al.* (2011) in ambrinoite. In fact, the

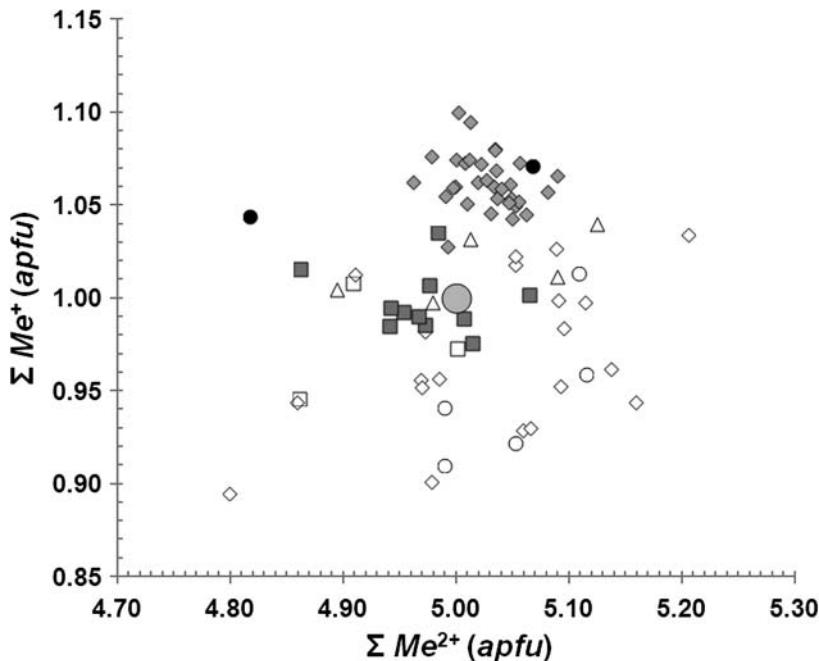


FIG. 2. Chemical variability of the occupancy of the tetrahedral site of galkhaite, expressed as a function of the sum of divalent cations ( $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ) versus the sum of monovalent cations ( $\text{Cu}^+$ ,  $\text{Ag}^+$ ), in atoms per formula unit (apfu). Same symbols as in Figure 1. The large grey circle represents the composition of ideal galkhaite, with a divalent:monovalent cation ratio of 5:1.

(Cs + Tl) deficit should be related to an excess of divalent cations at the tetrahedral site that was not observed. In addition, site scattering values refined for the Cs site (Table 5) do not suggest the presence of significant vacancies. Figure 3 shows the relation between Cs and Tl, confirming the substitution  $\text{Cs}^+ \rightarrow \text{Tl}^+$ , in accord with Makovicky (2005). In agreement with one spot analysis reported by Chen & Szymański (1981), the endmember composition  $(\text{Hg}_5\text{Cu})\text{TiAs}_4\text{S}_{12}$  is a potential new mineral species observed in the core of one crystal from Getchell. Additionally, these authors discussed the role of Tl in the crystal structure of galkhaite, suggesting that some  $\text{Tl}^{3+}$  can be hosted at the tetrahedral site. Their hypothesis was supported by the best fit given by the structural refinement carried out with minor Tl (0.08 apfu) at the Hg site. This amount of Tl corresponds to ca. 1.1 electron per formula unit. In our opinion, the same result could be achieved assuming the presence of 0.14 Ag apfu; this element was not sought by Chen & Szymański (1981), but its occurrence in galkhaite is rather common, as reported above. The highest Ag content observed in galkhaite from the Getchell mine during this work is 0.06 Ag apfu.

Taking into account the possible vacancy at the Cs site, the general chemical formula of galkhaite can be written as  $(\text{Hg}_{5-x}\text{Cu}_{1+x})\Sigma_6\text{Cs}_{1-x}\text{As}_4\text{S}_{12}$  ( $x \approx 0$ ).

Finally, the homovalent  $\text{As}^{3+} \rightarrow \text{Sb}^{3+}$  substitution takes place at the As site. The maximum amount of Sb reported so far in galkhaite is ca. 0.6 apfu (i.e., 0.58 apfu in galkhaite from Chauvay; analysis 5 of Pekov & Bryzgalov 2006), corresponding to an As/(As + Sb) atomic ratio of 0.85. The specimens examined in this study represent the As:Sb chemical variability very well, passing from the virtually Sb-free specimen from the Getchell mine (only 0.04 Sb apfu) to the Sb-enriched specimen from Gal-Khaya (0.56 Sb apfu). Notwithstanding an (As + Sb) deficit shown by the compositions of galkhaite from the Getchell mine and Signols, the crystal structure study points to a full occupancy of the As site, as shown by the site scattering values reported in Table 5.

## CONCLUSION

The crystallographic and chemical study of three specimens of galkhaite from different occurrences allows a better understanding of the crystal chemistry

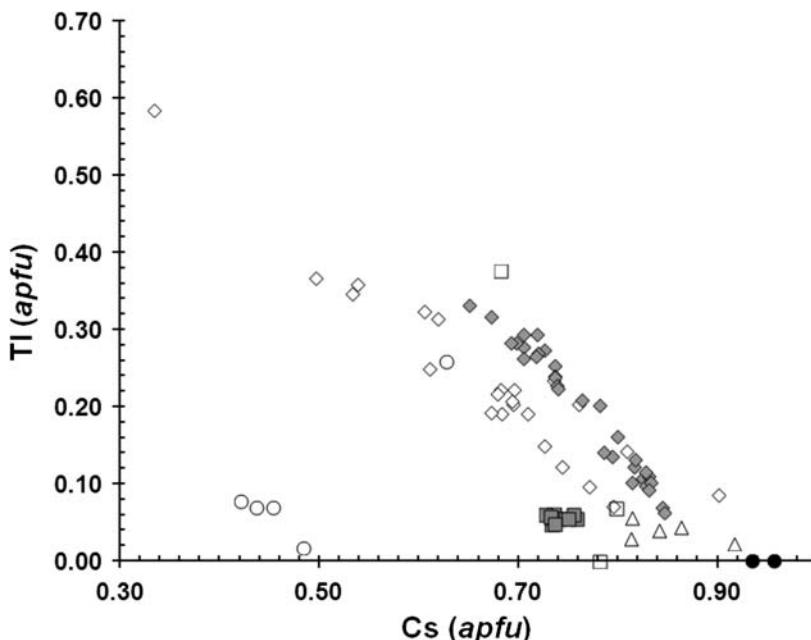


FIG. 3. Cs versus Tl, in apfu, in galkhaite. Same symbols as in Figure 1.

of this complex Hg-Cu-Cs sulfosalt mineral. The role of Cu as charge-compensating cation, balancing the introduction of Cs in the cavities of the galkhaite structure, has been clarified, and the possible existence of an “Ag-galkhaite” has been hypothesized. Further studies are required to understand the actual site population of the Cs site, which seems to show an intriguing variability. In fact, in addition to the existence of samples with Tl > Cs, representing a potential new mineral species, some specimens are characterized by a significant (Cs,Tl) deficit. Owing to the porous nature of galkhaite (Makovicky 2005), the possible occurrence of undetected compounds, e.g.,  $\text{NH}_4^+$  molecules, could not be excluded. In order to address this issue, a full crystal-chemical investigation of the (Cs,Tl)-deficient galkhaite from Khaidarkan described by Pekov & Bryzgalov (2006) seems to be mandatory.

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#### REFERENCES

- BIAGIONI, C., CIRIOTTI, M.E., AMBRINO, P., & BRIZIO, P. (2010) Secondo ritrovamento europeo di galkhaite: Cumbé Sürdè, Signols, Piemonte. *MICRO (UK Report)*, 118–123.
- BIAGIONI, C., BONACCORSI, E., PASERO, M., MOÉLO, Y., CIRIOTTI, M.E., BERSANI, D., CALLEGARI, A.M., & BOIOCCHI, M. (2011) Ambrinoite,  $(\text{K},\text{NH}_4)_2(\text{As},\text{Sb})_8\text{S}_{13}\cdot\text{H}_2\text{O}$ , a new mineral from Upper Susa Valley, Piedmont, Italy: the first natural ( $\text{K},\text{NH}_4$ )-hydrated sulfosalt. *American Mineralogist* **96**, 878–887.
- BIAGIONI, C., CAPALBO, C., & PASERO, M. (2013) Nomenclature tunings in the hollandise supergroup. *European Journal of Mineralogy* **25**, 85–90.
- BIAGIONI, C., BONACCORSI, E., MOÉLO, Y., & ORLANDI, P. (2014a) Mercury-arsenic sulfosalts from the Apuan Alps (Tuscany, Italy). III. Aktashite,  $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$ , and laffitite,  $\text{AgHgAsS}_3$ , from the Monte Arsiccio mine: occurrence and crystal structure. *Periodico di Mineralogia* **83**, 1–18.
- BIAGIONI, C., BONACCORSI, E., MOÉLO, Y., ORLANDI, P., BINDI, L., D'ORAZIO, M., & VEZZONI, S. (2014b) Mercury-arsenic sulfosalts from the Apuan Alps (Tuscany, Italy). II. Arsiccioite,  $\text{AgHg}_2\text{TLAs}_2\text{S}_6$ , a new mineral from the Monte Arsiccio mine: occurrence, crystal structure and crystal chemistry of the routhierite isotopic series. *Mineralogical Magazine* **78**, 101–117.

- BIAGIONI, C., MOÉLO, Y., & ORLANDI, P. (2014c) Lead-antimony sulfosalts from Tuscany (Italy). XV. (Tl-Ag)-bearing rouxelite from Monte Arsiccio mine: occurrence and crystal-chemistry. *Mineralogical Magazine* **78**, 651–661.
- BIAGIONI, C., ORLANDI, P., MOÉLO, Y., & BINDI, L. (in press) Lead-antimony sulfosalts from Tuscany (Italy). XVI. Carducciite,  $(\text{AgSb})\text{Pb}_6(\text{As},\text{Sb})_8\text{S}_{20}$ , a new Sb-rich derivative of rathite from the Pollone mine, Valdicastello Carducci: occurrence and crystal structure. *Mineralogical Magazine* (in press).
- BINDI, L., DOWNS, R.T., SPRY, P.G., PINCH, W.W., & MENCHETTI, S. (2012) A chemical and structural re-examination of fetelite samples from the type locality, Odenwald, southwest Germany. *Mineralogical Magazine* **76**, 551–566.
- BORISOV, S.V., MAGARILL, S.A., & PERVUKHINA, N.V. (2009) Characteristic features of crystal chemistry of natural mercury-containing sulfides and sulfosalts. *Journal of Structural Chemistry* **50**, 853–860.
- BOTINELLY, T., NEUERBURG, G.J., & CONKLIN, N.M. (1973) Galkhaite,  $(\text{Hg,Cu,Tl,Zn})(\text{As},\text{Sb})_2$  from the Getchell mine, Humboldt County, Nevada. *Journal of Research of the U.S. Geological Survey* **1**, 515–517.
- BRESE, N.E. & O'KEEFFE, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica* **B47**, 192–197.
- BRUKER AXS INC. (2004) APEX 2. Bruker Advanced X-ray Solutions, Madison, Wisconsin, United States.
- CHEN, T.T. & SZYMAŃSKI, J.T. (1981) The structure and chemistry of galkhaite, a mercury sulfosalt containing Cs and Tl. *Canadian Mineralogist* **19**, 571–581.
- CHEN, T.T. & SZYMAŃSKI, J.T. (1982) A comparison of galkhaite from Nevada and from the type locality, Khaidarkan, Kirgizia, Russia. *Canadian Mineralogist* **20**, 575–577.
- DIVIJKOVIĆ, V. & NOWACKI, W. (1975) Die Kristallstruktur von Galchait  $[\text{Hg}_{0.76}(\text{Cu},\text{Zn})_{0.24}]_{12}\text{Tl}_{0.96}(\text{AsS}_3)_8$ . *Zeitschrift für Kristallographie* **142**, 262–270.
- GRAESER, S., SCHWANDER, H., WULF, R., & EDENHARTER, A. (1995) Stalderite,  $\text{TiCu}(\text{Zn},\text{Fe},\text{Hg})_2\text{As}_2\text{S}_6$  – a new mineral related to routhierite: description and crystal structure. *Schweizerische Mineralogische und Petrographische Mitteilungen* **75**, 337–345.
- GRUZDEV, V.S., STEPANOV, V.I., SHUMKOVA, N.G., CHERNISTOVA, N.M., YUDIN, R.N., & BRYZGALOV, I.A. (1972) Galkhaite ( $\text{HgAsS}_2$ ), a new mineral from arsenic-antimony-mercury deposits of the U.S.S.R. *Doklady Akademie Nauk S.S.R.* **205**, 1194–1197 (in Russian).
- HATERT, F. & BURKE, E.A.J. (2008) The IMA-CNMNC dominant-constituent rule revisited and extended. *Canadian Mineralogist* **46**, 717–728.
- KAPLUNNIK, L.N., POBEDIMSKAYA, E.A., & BELOV, N.V. (1975) The crystal structure of galkhaite  $\text{HgAsS}_2$ . *Doklady Akademie Nauk S.S.R.* **225**, 561–563 (in Russian).
- MAKOVICKY, E. (2005) Micro- and mesoporous sulfide and selenide structures. *Reviews in Mineralogy & Geochemistry* **57**, 403–434.
- MAKOVICKY, E., FORCHER, K., LOTTERMOSER, W., & AMTHAUER, G. (1990) The role of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in synthetic Fe-substituted tetrahedrite. *Mineralogy and Petrology* **43**, 73–81.
- MOÉLO, Y., MAKOVICKY, E., MOZGOVA, N.N., JAMBOR, J.L., COOK, N., PRING, A., PAAR, W.H., NICEL, E.H., GRAESER, S., KARUP-MØLLER, S., BALIĆ-ŽUNIĆ, T., MUMME, W.G., VURRO, F., TOPA, D., BINDI, L., BENTE, K., & SHIMIZU, M. (2008) Sulfosalt systematics: a review. Report of the sulfosalt sub-committee of the IMA Commission on Ore Mineralogy. *European Journal of Mineralogy* **20**, 7–46.
- ORLANDI, P., MOÉLO, Y., MEERSCHAUT, A., PALVADEAU, P., & LÉONE, P. (2005) Lead-antimony sulfosalts from Tuscany (Italy). VIII. Rouxelite,  $\text{Cu}_2\text{HgPb}_{22}\text{Sb}_{28}\text{S}_{64}(\text{O,S})_2$ , a new sulfosalt from Buca della Vena mine, Apuan Alps: definition and crystal structure. *Canadian Mineralogist* **43**, 919–933.
- PEKOV, I.V. & BRYZGALOV, I.A. (2006) New data on galkhaite. *New Data on Minerals* **41**, 26–32.
- SHELDICK, G.M. (2008) A short history of SHELX. *Acta Crystallographica* **A64**, 112–122.
- VASIL'EV, V.I., PERVUKHINA, N.V., BORISOV, S.V., & MAGARILL, S.A. (2010) New data on the composition and crystal structure of galkhaite  $(\text{Hg,Cu})_6(\text{Cs,Tl})(\text{As},\text{Sb})_4\text{S}_{12}$ . *Geology of Ore Deposits* **52**, 662–668.
- WILSON, A.J.C. (1992) *International Tables for Crystallography, Volume C*. Kluwer, Dordrecht, Netherlands.
- ZELENSKI, M., GARAVELLI, A., PINTO, D., VURRO, F., MOÉLO, Y., BINDI, L., MAKOVICKY, E., & BONACCORSI, E. (2009) Tazieffite,  $\text{Pb}_{20}\text{Cd}_2(\text{As,Bi})_{22}\text{S}_{50}\text{Cl}_{10}$ , a new chloro-sulfosalt from Mutnovsky volcano, Kamchatka Peninsula, Russian Federation. *American Mineralogist* **94**, 1312–1324.

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