



# Thermodynamic modeling of native formation of Au–Ag–Cu–Hg solid solutions



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## ABSTRACT

It is difficult to interpret the significance of some types of gold alloys without thermodynamic data describing the Au–Ag–Cu–Hg systems. Literature data on the content of copper and mercury in native gold and silver and that of silver and gold in native copper and mercury from gold deposits of different genesis were collected and analyzed. Activity coefficients of the solid solutions in Au–Ag–Cu–Hg quaternary system were estimated. The corresponding calculation module prepared for a “Selektor-C” software package allows calculation of the composition of quaternary solid solutions depending on the change in T,P,X-parameters. Ore formation scenarios were modeled for two objects: i) “hydrothermal” – on the example of formation of quaternary solid solutions in hydrothermal conditions at the Aitik Au–Ag–Cu porphyry deposit (Sweden); ii) “hydrothermal-hypergene” – on the example of formation of Au–Cu intermetallics at the Wheaton Creek placer deposit (Canada). The approach described in our work can be used as an additional tool for the analysis of the genesis of gold deposits and estimation of formation conditions of natural solid solutions of noble metals that are in many cases the main carriers of ore components.

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## 1. Introduction

In addition to silver, other elements that form solid solutions with gold are copper and mercury (Chapman et al., 2011; Townley et al., 2003). Gold grains are natural alloys of Au, Ag, Cu, Hg, etc. in proportions that vary with the conditions of ore formation. Investigation into the solid solutions of the Au–Ag–Cu–Hg system is of great theoretical and applied importance in geochemistry, metallurgy, chemical technology and ecology. The minerals whose compositions fall within the Au–Ag–Cu–Hg system are native gold, silver and copper, as well as natural intermetallic compounds – auricupride, cuproauride, tetra-auricupride, eugenite, luanheite, moschellandsbergite, paraschachnerite, schachnerite, belendorffite, kolymite and weishanite (Table 1). These names of minerals have been approved by IMA (Downs et al., 2007). Mercury occurs as a liquid and does not satisfy the normal criteria to be a valid mineral. The compositions of binary solid solutions and stable crystallographic phases known in the Au–Cu, Au–Hg, Cu–Hg and

Ag–Hg systems (ASM metals, 1992) are given in Table 2. Compositional data on metallic ternary alloys that form at ore deposits worldwide were compiled in literature (Bonev et al., 2002; Townley et al., 2003; Chudnenko and Pal'yanova, 2013a). Bonev et al. (2002) show that native gold of the Chelopech high-sulfidation volcanic-hosted epithermal Au–Cu deposit (Bulgaria) is characterized by a low content of silver to 5.27 wt.% and minor copper to 0.53 wt.%, but the increase in silver content to 33.8 wt.% is related to the late polymetallic Pb–Zn stage. Study of native gold composition from epithermal, Au-rich porphyry and Au-rich porphyry Cu systems indicated Au–Ag–Cu contents to be the best discrimination tool for these different types of Au-bearing deposits (Townley et al., 2003). Data on the compositions of natural Au–Ag amalgams evidence that the amount of mercury is no more than 20 wt.% in the gold-rich ternary Ag–Au–Hg system and less than 37–38 wt.% in the silver-rich system (Chudnenko and Pal'yanova, 2013a).

Deposits that contain native gold with mercury and copper are also abundant. The quaternary system Au–Ag–Cu–Hg has not been studied experimentally but solid solutions and intermetallic compounds occur at numerous primary gold deposits and placers in different regions of the world (Dumula and Mortensen, 2002;

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**Table 1**

The names and crystallographic data of minerals accepted IMA (Downs et al., 2007) in the Au–Ag–Cu–Hg system.

Mineral names	Chemistry	Crystal system	Space group
Gold	Au	Cubic	$Fm\bar{3}m$
Silver	Ag	Cubic	$Fm\bar{3}m$
Copper	Cu	Cubic	$Fm\bar{3}m$
Auricupride	$Cu_3Au$	Cubic	$Pm\bar{3}m$
Cuproauride	$Cu_3Au$	—	—
Tetra-auricupride	CuAu	—	—
Eugenite	$Ag_{11}Hg_2$	Cubic	$Fm\bar{3}m$
Luanheite	$Ag_3Hg$	Hexagonal	—
Moschellandsbergite	$Ag_3Hg_3$	Cubic	$I23$
Paraschachnerite	$Ag_{1.2}Hg_{0.8}$	Orthorhombic	—
Schachnerite	$Ag_{1.1}Hg_{0.9}$	Hexagonal	—
Belendorffite	$Cu_7Hg_6$	Hexagonal	$R\bar{3}m$
Kolymite	$Cu_7Hg_6$	Cubic	$I\bar{4}3m$
Weishanite	$(Au,Ag)_{1.2}Hg_{0.8}$	Hexagonal	$P6_3/mmc$

Kucha and Raith, 2009; Sammelin et al., 2011; Spiridonov and Pletnev, 2002). Compositional data on metallic quaternary alloys in the system Au–Ag–Cu–Hg were compiled for the first time in this study. Formation of native gold with admixtures of copper and mercury in nature refers to hydrothermal ore formation, supergene processes during weathering of gold and copper deposits, and technogenic processes during ore extraction (Naumov and Naumova, 2014; Sammelin et al., 2011; Spiridonov and Pletnev, 2002) that involve wide ranges of  $T,P$ -parameters.

Physicochemical modeling of ore-forming, technogenic and metallurgical processes with the formation of gold alloys of various compositions, i.e. containing not only silver but copper and mercury admixtures as well, requires the knowledge of standard thermodynamic constants of solid solutions of the Au–Ag–Cu–Hg system. Estimations of thermodynamic properties of solid solutions of six binary subsystems (Au–Ag, Au–Cu, Ag–Cu, Ag–Hg, Au–Hg, Cu–Hg) and two ternary subsystems (Au–Ag–Cu, Au–Ag–Hg) of the quaternary system Au–Ag–Cu–Hg have been already performed in (Chudnenko and Pal'yanova, 2013a, b; 2014; Liu et al., 2012; Palyanova, 2008). Experimental data on the stability of solid phases in the system Ag–Cu–Hg for 37 °C are reported in (Kubaschewski, 1988). However, standard thermodynamic constants of the ternary Au–Cu–Hg, Ag–Cu–Hg and the quaternary Au–Ag–Cu–Hg solid solutions are unknown.

The aim of this work is to summarize data on the content of copper and mercury in native gold and silver, as well as silver and gold in native copper and mercury and to estimate the

thermodynamic functions of ternary Au–Cu–Hg and Ag–Cu–Hg and quaternary Au–Ag–Cu–Hg solid solutions. One of the tasks of the research was to prepare the calculation block for the program “Selektor-C” (Chudnenko, 2010) for carrying out model calculations in the systems containing Au, Ag, Cu and Hg.

## 2. Minerals of the Au–Ag–Cu–Hg system

### 2.1. Compilation of metallic alloys at ore deposits

Naturally occurring Au–Ag alloys commonly contain varying amounts of copper and mercury and, more rarely, other elements (Sb, Se, Te, Bi, Ni, Fe) (Boyle, 1979; Knight and Leitch, 2001; Petrovskaya, 1993). We have collected and summarized literature data on the compositions of quaternary solid solutions and intermetallic compounds in the system Au–Ag–Cu–Hg, as well as binary and ternary solid solutions and intermetallic compounds associated with them (Tables 1S and 2S (Supporting Material)). Table 3 shows the compositions of quaternary solid solutions and intermetallic compounds, as well as host rocks, mineral associations, and physicochemical conditions of formation at a wide range of deposit types and settings.

Presence of copper and mercury in native gold and silver was established at many deposits related to hyperbasic and basic rocks (Murzin et al., 2006; Spiridonov and Pletnev, 2002). Spiridonov and Pletnev (2002) report that at the Zolotaya Gora (Urals, Russia) deposit there occur different varieties of Au–Ag–Cu–Hg solid solutions – minerals of the group of copper gold, native copper and Au–Ag amalgams. They determined phases of complex composition  $Cu_2(Au,Ag,Hg)_3$  with admixtures of silver from 0.64 to 0.77 wt.% and mercury to 0.08 wt.%. The compositions of other Au–Cu alloys vary in rather narrow ranges and contain admixtures of silver and mercury (Table 3). Some of these alloys are very well described by  $Cu_3Au$ , CuAu and  $CuAu_3$  (ASM handbook, 1992; Chang et al., 1977; Ozolins et al., 1998). Au–Ag amalgams are associated with Au–Cu alloys and contain to 1 wt.% Cu (Table 3). In the Eastern ore body of the Zolotaya Gora deposit, in parageneses with selenium-bearing chalcocite and Ag–Au amalgams, there occur tabular inclusions of composition  $Cu_7Hg_6$  (probably kolymite), which in the zone of weathering turned into a porous aggregate of native copper containing to 1 wt.% Hg (Spiridonov and Pletnev, 2002). Gold mineralization at the Zolotaya Gora deposit is attributed to the formation processes of rodingites, which, according to studies of fluid inclusions, take place at temperature no less than 400 °C and moderate pressure 1–3 kbars with participation of

**Table 2**

The stable crystallographic phases and their crystallographic data in the Au–Ag–Cu–Hg systems (ASM handbook of alloys, 1992).

Phases	Composition, wt.%	Composition, at. Fraction	Crystal system	Space group	T of stability, °C
(Ag,Au) ss	0 to 100 (Ag)	$Au_{1.0}Ag_{0.0}-Au_{0.0}Ag_{1.0}$	Cubic	$Fm\bar{3}m$	$\leq 961.83-1064.43$
(Au,Cu) ss	0 to 100 (Cu)	$Au_{1.0}Cu_{0.0}-Au_{0.0}Cu_{1.0}$	Cubic	$Fm\bar{3}m$	$\leq 1064.43-1084.87$
$Au_3Cu$ ss	3 to 16.8 (Cu)	$Au_{0.91}Cu_{0.09}-Au_{0.62}Cu_{0.38}$	Cubic	$Pm\bar{3}m$	$\leq 240$
AuCu(I) ss	19 to 30 (Cu)	$Au_{0.58}Cu_{0.42}-Au_{0.43}Cu_{0.57}$	Tetragonal	$P4/mmm$	$\leq 385$
AuCu(II) ss	16.8 to 35 (Cu)	$Au_{0.62}Cu_{0.38}-Au_{0.38}Cu_{0.62}$	Orthorhombic	$Imma$	$\leq 410$
$AuCu_3(I)$ ss	40 to 58 (Cu)	$Au_{0.33}Cu_{0.67}-Au_{0.19}Cu_{0.81}$	Cubic	$Pm\bar{3}m$	$\leq 390$
$AuCu_3(II)$ ss	39 to ? (Cu)	$Au_{0.34}Cu_{0.66}-?$	Tetragonal	$Pmm$	$\leq 285$
(Ag,Cu) ss	0 to 8.8 (Cu)	$Ag_{1.0}Cu_{0.0}-Ag_{0.86}Cu_{0.14}$	Cubic	$Fm\bar{3}m$	$\leq 961.83$
(Cu,Ag) ss	92.0 to 100 (Cu)	$Ag_{0.05}Cu_{0.95}-Ag_{0.0}Cu_{1.0}$	Cubic	$Fm\bar{3}m$	$\leq 1084.87$
(Cu,Hg)	0 to ? (Hg)	$Cu_{1.0}Hg_{0.0}-?$	Cubic	$Fm m$	$\leq 1084.87$
$Cu_7Hg_6$	73 (Hg)	$Cu_{0.54}Hg_{0.46}$	Rhombohedral	$R m$	$\leq 128$
(Au,Hg) ss	0 to 20.1 (Hg)	$Au_{1.0}Hg_{0.0}-Au_{0.80}Hg_{0.20}$	Cubic	$Fm\bar{3}m$	$\leq 1064.43$
$\alpha$ -(Au,Hg) ss	16.2 to 23 (Hg)	$Au_{0.84}Hg_{0.16}-Au_{0.77}Hg_{0.23}$	Hexagonal	$P6_3/mmc$	$\leq 419$
$\zeta$ -(Au,Hg) ss	21 to 26 (Hg)	$Au_{0.79}Hg_{0.21}-Au_{0.74}Hg_{0.26}$	Hexagonal	$P6_3/mmc$	$\leq 122$
(Ag,Hg) ss	0 to 52.5 (Hg)	$Ag_{1.0}Hg_{0.0}-Ag_{0.63}Hg_{0.37}$	Cubic	$Fm\bar{3}m$	$\leq 961.93$
$\zeta$ -(Ag,Hg) ss	58.9 to 61.3 (Hg)	$Ag_{0.57}Hg_{0.43}-Ag_{0.54}Hg_{0.46}$	Hexagonal	$P6_3/mmc$	$\leq 358.82$
$\gamma$ -(Ag,Hg) ss	70.0 to 71.0 (Hg)	$Ag_{0.44}Hg_{0.56}-Ag_{0.43}Hg_{0.57}$	Orthorhombic	$I23$	$\leq 127$

**Table 3**  
Typical compositions of native Au–Ag–Hg–Cu alloys, mineral associations and host rocks and physicochemical conditions of formation at wide range of deposit types and settings (literature data).

Deposits (localities)/Ref. <sup>a</sup>	Content of element (wt %)/Formula (mol. fraction), additional impurities				Host rocks/mineral associations	T; P; sal. (wt.%NaCl-eq.)
	Au	Ag	Cu	Hg		
<b>Magmatic–hydrothermal deposits</b>						
Zolotaya Gora (Urals, Russia)/1, 2	86.29–88.24	1.56–1.93	11.17–12.89	0–0.24	Chloritoliths/phase Cu <sub>2</sub> (Au,Ag,Hg) <sub>3</sub>	230–470 °C; 1–2 kbar; -
	<b>CuAu<sub>3</sub></b> (Au <sub>0.66–0.70</sub> Ag <sub>0.02–0.03</sub> Cu <sub>0.27–0.31</sub> Hg <sub>0–0.02</sub> )					
	72.4–76.15	0.22–0.65	24.94–25.38	0–0.26	Rodingites/Cu, Mch, Chc, Mt	
	<b>Cuproauride CuAu</b> (Au <sub>0.48–0.49</sub> Cu <sub>0.51–0.52</sub> Ag <sub>0–0.01</sub> Hg <sub>0–0.01</sub> )					
	80.75–83.64	0.64–0.77	17.06–18.02	0–0.08	- “ -/Cup, Cat	
	<b>Cu<sub>2</sub>(Au,Ag,Hg)<sub>3</sub></b> (Au <sub>0.59–0.62</sub> Cu <sub>0.36–0.41</sub> Ag <sub>0–0.01</sub> Hg <sub>0–0.01</sub> )					
	50.06–52.14	0–0.21	48.22–49.88	0–0.31	- “ -/Cu, Mch, Chc, Mt	
	<b>auricupride Cu<sub>3</sub>Au</b> (Au <sub>0.24–0.26</sub> Ag <sub>0–0.01</sub> Cu <sub>0.74–0.75</sub> Hg <sub>0–0.01</sub> )					
	24.13–48.51	41.66–59.26	0.24–0.97	2.48–14.26	- “ -/Aur, CuAu <sub>3</sub>	
	<b>Ag–Au–Cu–Hg alloys</b> (Au <sub>0.16–0.36</sub> Ag <sub>0.56–0.73</sub> Cu <sub>0.01–0.02</sub> Hg <sub>0.02–0.10</sub> )					
	0.18–0.56	≤0.23	98.88–99.33	≤0.37	- “ -/Aur, Mch, Chc, Mt	
	<b>Cu</b> (Cu <sub>0.997–0.998</sub> Au <sub>0.001–0.002</sub> Ag <sub>0–0.001</sub> Hg <sub>0–0.001</sub> )					
<b>Agardag massif (Tuva, Russia)/2, 3</b>	74.63–77.38	0.12–0.34	23.41–24.94	0.000	Ab-Px rodingites, nephritoids/Mch	400–500 °C; 1–2 kbar; -
	<b>AuCu</b> (Cu <sub>0.487–0.502</sub> Au <sub>0.492–0.513</sub> Ag <sub>0.001–0.003</sub> )					
	48.12–59.89	36.91–51.47	0.14–0.34	0.47–1.58	Rodingites/Amf, Ab, Chc, Py, Ccp, Mt	230–310 °C; -; -
	<b>Au–Ag–Hg–Cu alloys</b> (Au <sub>0.654–0.715</sub> Ag <sub>0.397–0.465</sub> Cu <sub>0.001–0.002</sub> Hg <sub>0.004–0.008</sub> )					
<b>Au–Cu porphyry deposits (magmatic–hydrothermal and metamorphosed)</b>						
<b>Aitik (Sweden)/4, 5</b>	96.99–97.27	0–0.04	0–0.01	0–0.25	Bt-gneiss/Kfs, Bt, Pl, Q,Ccp, Py	I stage 500–600 °C; 4–5 kbar; 16–57
	<b>I Au–Cu–Ag–Hg alloys</b> (Au <sub>0.990–0.998</sub> Ag <sub>0–0.001</sub> Cu <sub>0–0.008</sub> Hg <sub>0.001–0.002</sub> )					
	3.69–4.03	59.32–60.10	0.02–0.04	33.71–35.40	Grt-Bt-gneiss/Q, Turm, Ep, Kfs, Ab, Py	II stage 300 °C; 3 kbar; 38
	<b>II Ag–Hg–Cu–Au alloys</b> (Au <sub>0.015–0.027</sub> Ag <sub>0.741–0.742</sub> Cu <sub>0.001–0.002</sub> Hg <sub>0.227–0.235</sub> ) (Sb, Te)					
	13.81–41.23	45.57–68.58	0–0.08	8.50–14.04	Py,Ccp, Fe-oxides	III stage 200–500 °C; 1 kbar; -
	<b>III Au–Ag–Hg–Cu alloys</b> (Au <sub>0.091–0.309</sub> Ag <sub>0.624–0.821</sub> Cu <sub>0–0.002</sub> Hg <sub>0.065–0.087</sub> ) (Sb, Te, Bi)					
<b>Epithermal Au–Ag deposits</b>						
Tsugu Au–Sb vein deposit (Japan)/6	79.95–93.09	6.52–10.91	0.03–0.08	0.07–8.53	Q-Ser veins/Po, Ga, Sph, Stb, Jam, Cub, Py, Asp, Ow	275–295 °C; -; -
	<b>Au–Ag–Hg–Cu alloys</b> (Au <sub>0.738–0.885</sub> Ag <sub>0.113–0.184</sub> Cu <sub>0.001–0.002</sub> Hg <sub>0.001–0.077</sub> )					
	79.96–98.13	1.38–19.49	0–0.11	0–0.14	Q-veins and veinlets/Q, Py	I stage 125–450 °C; -; 3–10
	<b>Au–Ag–Cu–Hg alloys A1</b> (Au <sub>0.692–0.970</sub> Ag <sub>0.025–0.308</sub> Cu <sub>0–0.003</sub> Hg <sub>0–0.001</sub> ) (Fe, S, Bi, Te, Se)					
	75.34–97.5	1.71–23.94	0	0–0.12		
	<b>Au–Ag–Cu–Hg alloys A2</b> (Au <sub>0.633–0.968</sub> Ag <sub>0.031–0.367</sub> Hg <sub>0–0.001</sub> ) -,-					
	70.95–97.21	3.48–28.53	0–0.44	0–0.23	- “ -/Q, Py, Ga, Sph, Ccp	II stage 25–300 °C; -; 2–29
	<b>Au–Ag–Cu–Hg alloys B1</b> (Au <sub>0.577–0.924</sub> Ag <sub>0.060–0.423</sub> Cu <sub>0–0.013</sub> Hg <sub>0–0.002</sub> ) -,-					
	72.53–85.35	13.75–26.07	0–2.56	0.03–0.16		
	<b>Au–Ag–Cu–Hg alloys B2</b> (Au <sub>0.604–0.720</sub> Ag <sub>0.212–0.396</sub> Cu <sub>0–0.067</sub> Hg <sub>0–0.001</sub> ) -,-					
	97.83–100.00	0–1.82	0–0.23	0.01–0.12	altered volcanic rock	-
	<b>Au–Ag–Cu–Hg alloys C</b> (Au <sub>0.965–0.992</sub> Ag <sub>0–0.035</sub> Cu <sub>0–0.007</sub> Hg <sub>0–0.001</sub> ) -,-					
<b>Sedimentary hydrothermal copper deposits (low-temperature hydrothermal and supergene environments)</b>						
Larzenbach St. Veit im Pongau (Austria)/9	54.74–96.79	0.06–25.59	1.05–22.07	0.06–21.25	phyllites, black schists/Tet, Auos, Ccp, Asp, Cu–Fe oxide	70–250 °C; -; -
	<b>Au–Ag–Cu–Hg alloys</b> (Au <sub>0.43–0.94</sub> Ag <sub>0–0.37</sub> Cu <sub>0–0.47</sub> Hg <sub>0–0.18</sub> ) (Pt, Pd, Fe, As, Sb, S, Ni)					

**Abbreviation of minerals:** Q – quartz, Ab – albite, Bt – biotite, Ep – epidote, Kfs – K-feldspar, Pl – plagioclase, Ser – micro flake muscovite, Cal – calcite, Chl – chlorite, Px – pyroxene, Grt – garnet, Turm – tourmaline, Sph – sphalerite, Asp – arsenopyrite, Aur – auricupride (Cu<sub>3</sub>Au), Cup – cuproauride (CuAu), Cu – native copper, Mt – magnetite, Mch – maucherite (Ni<sub>11</sub>As<sub>8</sub>), Mo – molybdenite, Chc – chalcocite (Cu<sub>2</sub>S), Ccp – chalcopyrite, Py – pyrite, Po – pyrrothite, Pnt – pentlandite ((Fe,Ni)<sub>9</sub>S<sub>8</sub>), Pz – petzite, Rar – realgar, Tet – tetrahedrite, Ten – tennantite, Jam – jamesonite, Cub – cubanite, Brnt – bornite, Ow – owoyheeite, Stb – stibnite, Aub – austrobitite, Crd – criddleite (TlAu<sub>2</sub>Sb<sub>10</sub>S<sub>10</sub>), Clv – Calaverite, Ptz – petzite, Bar – barite, Hem – hematite, As – native arsenic, Te – native tellur, Auos – Au-oxy-sulphides.

<sup>a</sup> **References:** 1 – Spiridonov and Pletnev, 2002; 2 – Murzin et al., 2006; 3 – Kudryavtseva and Kudryavtsev, 2003; 4 – Sammelin et al., 2011; 5 – Wanhainen et al., 2012; 6 – Shikazono and Shimizu, 1988; 7 – Carrillo Rosua et al., 2002; 8 – Morales et al., 2000; 9 – Kucha and Raith, 2009.

water fluids enriched with reduced gases, mainly hydrogen and methane, and have a low content of carbon dioxide (Murzin et al., 2006). Data on the restoration of isotopic fluid composition during formation of gold-bearing rodingites of Zolotaya Gora evidence participation of water of marine origin and ultrabasic and basic magmatic rocks.

Data are available on the occurrences of copper gold in

rodingites within the Agardag massif of alpine-type hyperbasic rocks (Tuva, Russia) (Murzin et al., 2006). Copper gold represented by tetra-auricupride was reported to occur along with native gold containing major amounts of Ag (36.91–51.47 wt.%) and minor amounts of Cu (0.14–0.34 wt.%) and Hg (0.47–1.58 wt.%) (Kudryavtseva and Kudryavtsev, 2003). Deviation of tetra-auricupride from stoichiometric composition is slight and Ag

admixture do not exceed 0.34 wt.% (Table 3).

Coexistence of high mercury and low copper concentrations in Au–Ag alloys was described at the Aitik Cu–Au–Ag porphyry deposit, Gällivare area, Northern Sweden (Sammelin et al., 2011). The composition of native gold in the Aitik deposit varies substantially. It occurs in many different associations in mineralization styles (Table 3): I – the richest in Au and II and III – the richest in Hg and Ag. Native gold is commonly found in the matrix of the bedrock and in quartz-tourmaline veins with sulfides. The overall most common minerals associated with native gold are K-feldspar, biotite, plagioclase, quartz, chalcopyrite and pyrite. Magmatic–hydrothermal and metamorphic processes responsible for the diversity in mineralization styles within the Aitik ore body have probably also influenced the variable character of native gold.

Zaikov et al. (2012) reported that Au–Ag alloys at several Au-rich volcanogenic massive sulfide deposits of the Ural (Mechnikovskoe, Altyn-Tashskoe, and Tash-Tau) contained to 2.1 wt.% Hg, whereas the content of Cu was no more than 1.83 wt.% (Table 1S (Supporting Material)). Gold occurs as inclusions, thin veinlets in bornite and galenite, and at the contacts of fractured crystals of pyrite, chalcopyrite, barite and other minerals of submarine hypergenesis (Zaikov and Melekestseva, 2011).

The chemical compositions of native gold at the epithermal Au–Sb vein Tsugu deposit can be expressed as  $Au_{0.738-0.885}Ag_{0.113-0.184}Cu_{0.001-0.002}Hg_{0.001-0.077}$  (Table 3). Homogenization temperatures of fluid inclusions are 275–295 °C for the stage of gold mineralization (Shikazono and Shimizu, 1988). Pyrrhotite, cubanite, Fe-sphalerite, and arsenopyrite, present in association with native gold, suggest relatively low  $f_{S_2}$  conditions.

In the Fe–Cu–Au vein epithermal Palai–Islica deposit, in Southeastern Spain, three types (A1,A2; B1,B2; C) of Au–Ag–Cu–Hg alloys were found in association with sulfide mineralization (particularly Fe sulfides) (Table 3). The chemical characteristics of B-type correspond to Au–Ag alloys with Ag content higher than in A-type alloys. C-type corresponds to native gold with a very low content of Ag (0–1.82 wt.%). There are no considerable differences in minor element contents of Cu and Hg with native gold of A and B types. Grains of Au–Ag alloys (A- and B-types) occur with pyrite in mineralized veins, and grains of native gold (C-type) are associated with the areas of massive silicification at the uppermost levels of the deposit (Carrillo Rosua et al., 2002). Morales Ruano et al. (2000) demonstrated the existence of different fluids in the Palai–Islica deposit. A fluid with low salinity (range mainly from 3 to 10 wt.% NaCl eq.) and high variations in temperature (125–450 °C) is found throughout the deposit. The geochemical anomalies in Au, Ag and other elements (Cu, Zn, Pb, Bi, As, Sb and Cd) are associated with another fluid characterized by high variation in salinity (2.0–29.3 wt.% NaCl eq.) over a temperature range of 200 and 300 °C.

High copper concentrations were detected in Au–Ag alloys at the sedimentary hydrothermal copper deposits of the Greywacke Zone (Austria). Kucha and Raith (2009) distinguished five types of Au–Ag alloys with Hg and (or) Cu. General ranges of variations for all 4 elements are given in Table 3 and detailed ranges are listed in Table 1S (Supporting Material). Primary gold of type 1 is present in massive non-fractured tetrahedrite and Cu content is below detection limit. Native gold of type 2 is present in microfractures in tetrahedrite together with pyrite, gersdorffite, chalcopyrite, cubanite, arsenopyrite and quartz. At Larzenbach these Au–Ag alloys contain to 21.25 wt.% Hg and 3.88 wt.% Cu. An unnamed  $Ag_2Au_3Hg$  phase (type 3) occurs in fractures in tetrahedrite at Mitterberg. Au–Ag alloys of type 4 intergrow with oxysulfides from the hydrothermal paragenesis. Type 5 of Au–Ag alloys from the supergene weathering paragenesis is characterized by the highest

Cu contents from 4.6 to 22.07 wt.%. This secondary native gold is intergrown with oxysulfides, cuprite, limonite and, less often, malachite. It is variable in Ag (<0.06 to 14.87 wt.%), Hg (<0.06 to 4.68) and may contain considerable amounts of Sb (1.04–15.73). Fluid inclusions in tetrahedrite are of low to moderate salinity and homogenization temperatures range between 85 and 190 °C. Cu-rich secondary native gold and the weathering mineral assemblages formed during hypergene alteration. Transport, mobilization and redeposition of Au, Ag, Cu and Hg seem to be related to low-temperature hydrothermal and hypergene environments.

A great number of data is reported in literature on the composition of placer native gold (Table 2S (Supporting Material)). The placer deposits are related to primary lode deposits. Microprobe analysis of the chemical composition of alluvial gold from the Mayo within the valley of the present-day Lightning Creek river (territory of Yukon, Canada) revealed wide variations in Ag admixture from 0 to 44.1 wt.%, presence of Cu to 1.4 wt.% and, rarely, Hg to 0.9 wt.% (Naumov et al., 2010).

Data from M. Higgins (2012) compositional studies of placer gold grains in the west-central Yukon show variations in the range of 10–35 wt.% Ag, and admixtures no more than 0.07 wt.% Cu. The contents of mercury are higher than that of copper and in places reach 5.8 wt.% in grain rims. Gold grains from the Black Hills Creek area (Western Yukon) are characterized by 8–20 wt.% Ag and 0.2–0.5 wt.% Hg and 0–0.05 wt.% Cu (Dumula and Mortensen, 2002). Gold grains from Eureka were found to have 30–50 wt.% Ag and 0.3–0.7 wt.% Hg and <0.02 wt.% Cu (Dumula and Mortensen, 2002). Gold grains from Henderson Dome contain 20–50 wt.% Ag and 0.3–3 wt.% Hg (Bond and Chapman, 2007). In gravel deposits on the Northern outskirts of Whitecourt, North-Central Alberta (Canada), the placer gold ranges 21–45 wt.% Ag in the cores of grains but sharply defined rims have a much lower content: 2–6 wt.% Ag with Cu < 0.1 wt.% (Mudaliar et al., 2007). Chapman et al. (2011) established a type of gold with highly variable Ag and Hg to a maximum of 11 wt.%. The new type of native gold was found only in placers in the middle and lower Indian River. It is distinguished by slightly elevated 0.05–0.17 wt.% Cu together with low 5–9 wt.% Ag contents. Inclusions of Bi minerals, Cr-bearing magnetite and molybdenite within gold suggest an intrusion-related source.

The placer native gold from the San Luis Range of Argentina is a good example of natural environment with a limited anthropogenic impact (Marquez-Zavalía et al., 2004). For the uncontaminated samples the chemical compositions in the core commonly range from 15 to 47 wt.% Ag, whereas Cu and Hg values are almost consistently close to the lower limit of detection (0.06 wt.% for Cu and 0.12 wt.% for Hg). The anthropogenic Hg-contaminated samples (from core to rim) have chemical compositions ranging from 5 to 42 wt.% Ag, 2 to 31 wt.% Hg, and Cu content is under or very close to the lower limit of detection.

The placer native gold from the Wheaton Creek deposit (British Columbia, Canada) has a high copper content up to 23.23 wt.% and low mercury content 0.08 wt.% (Knight and Leitch, 2001). Most grains contain Au–Ag alloys of more than one composition. The differing compositions outline a variety of textural relationships among grains. The textures can be described in terms of three basic types: massive, blebby and exsolved. For Au–Cu compositions between  $CuAu$  and  $Cu_2Au$ , massive phases are generally closest to  $Au_{0.52}Cu_{0.48}Ag_{0.003}$ , followed by blebby and exsolved phases with increasing Au content and decreasing Cu content from  $Au_{0.66}Cu_{0.32}Ag_{0.02}$  to  $Au_{0.72}Ag_{0.16}Cu_{0.10}Hg_{0.0003}$ .

Alluvial tetra-auricupride with traces of Ag and Hg, associated with native gold, was found at Rio the Misery (Switzerland) (Meisser and Brugger, 2000). The native gold particle included in the tetra-auricupride contained significant but variable contents of

Cu and Hg and was poor in Ag. Native gold with traces of Cu to 0.05 wt.% and of Hg to 0.88 wt.% from La Cerjaulé river (Switzerland) (Meisser and Brugger, 2000) shows a core to rim zoning. The rim is enriched in Au and depleted in Ag relative to the core. The content of Hg is higher in the rim than in the core of the particle.

Barkov et al. (2009) described zoned amalgams of Au and Ag with traces of Cu to 0.07 wt.% in a placer deposit associated with the Tulameen – Similkameen river system (British Columbia, Canada). The observed compositions are limited by the range  $Au_{0.390-0.538}Ag_{0.264-0.461}Cu_{0-0.02}Hg_{0-0.293}$ . These amalgams formed at the expense of primary Au–Ag alloys which are present as relics in the core  $Au_{0.54-0.55}Ag_{0.45-0.46}$ .

Variations from 0.04 to 10.44 wt.% Cu and 0.21 to 28.72 wt.% Hg were found in native gold from technogenic dumps of the Isovskii (Ural, Russia) placer along with the phases of the Au–Cu system, which are similar in composition to  $Au_3Cu$  (Naumov and Naumova, 2014).

## 2.2. Distribution of components in solid solution

Au–Ag–Cu–Hg alloys can be found in various settings such as magmatic–hydrothermal, Au-rich volcanogenic massive sulfide, Au–Cu porphyry, epithermal Au–Ag deposits and a number of lower temperature hydrothermal ore deposits and placer Au deposits world-wide. The element compositions of Au–Ag–Cu–Hg alloys depend on ore-forming conditions ( $P, T, f_{O_2}, f_{S_2}, pH$ , etc.) and concentration processes. Most of Au–Ag–Cu–Hg natural solid solutions occur at the deposits formed at temperatures 25–600 °C. Despite the variety of their formation conditions and presence of various accompanying mineral associations, the ratios of Au, Ag, Cu and Hg have limited variations. The continuity of solid solutions is the result of limited solubility of metals in each other in basic binary solutions (Table 4) and rather low temperatures of the existence of melt in the Hg-containing systems. A list of stable phases is given in Tables 1 and 2

Estimation of the distribution of components in ternary solid solutions yielded the following data on the maximum concentration of metals: for Au–Ag–Hg alloy the limit of Cu content is 22.1 wt.% (mercury concentration 2.3 wt.%) or 48.3 wt.% (mercury concentration 0–0.15 wt.%) (Knight and Leitch, 2001), limit of Hg content in Au–Ag–Cu alloy compositions is 35.4 wt.% (Sammelin et al., 2011).

When studying the stability of natural solid solutions of the quaternary system under consideration, we used the collected database from published data that included 351 analyses of natural Au–Ag–Cu–Hg alloys and compounds (Tables 1S and 2S

**Table 4**  
Reciprocal solubility of metals in atomic percentage (Lyakishev, 1996).

Solvent	Soluble			
	Au	Ag	Cu	Hg
Au	–	100	100	19.8
Ag	100	–	14.1	37.3
Cu	100	4.9	–	0.6 (200°C), 1 (300°C), 1.5 (400°C), 3 (500°C), 4 (600°C), 5 (max)
Hg	<1	0.07 (20 °C) 0.41 (100 °C) 1.8 (200 °C) 2.4 (300 °C) 19 (400 °C) 38.5 (500 °C)	0.01 (25°C) 3.6 (550 °C)	–

(Supporting Material)) reported for different types of deposits discussed in Chapter 2.1. The ternary diagrams Au–Ag–Cu, Au–Ag–Hg, Ag–Cu–Hg and Au–Cu–Hg of the quaternary system Au–Ag–Cu–Hg represented in Figs. 1–4 are based on these data. The amount of each metal reported in wt.% in the source was recalculated to mole fractions the total sum of which is 1.

The Au–Ag–Cu system is the best studied (Fig. 1) among the investigated ternary systems. The Ag–Cu miscibility gap extends into the ternary Cu–Ag–Au system (Prince et al., 2006). Thus, related composition–temperature ranges in this isotherm in fact reflect metastable equilibria (shown by a dashed line). All points on the diagram are below 400 °C isotherm. Such distribution of metals in the system Cu–Ag–Au was obtained by Knight and Leitch (2001) in the analysis of 258 Cu-rich phases for placer gold particles from Southern British Columbia (Canada).

Distribution of metals in the ternary Ag–Au–Hg system was analyzed in a number of articles (Basu et al., 1981; Healy and Petruk, 1990; Shikazono and Shimizu, 1988). The determining part in the identification of the region of solid solutions belongs to the liquid–solid phase boundary. Although some authors (Basu et al., 1981; Shikazono and Shimizu, 1988) refer all points of analyses only to the region of formation of solid solutions, with a greater number of various samples taken into account, some points can probably fall into the field of existence of liquid + solid solution (Healy and Petruk, 1990). It is this distribution that we obtained (Fig. 2).

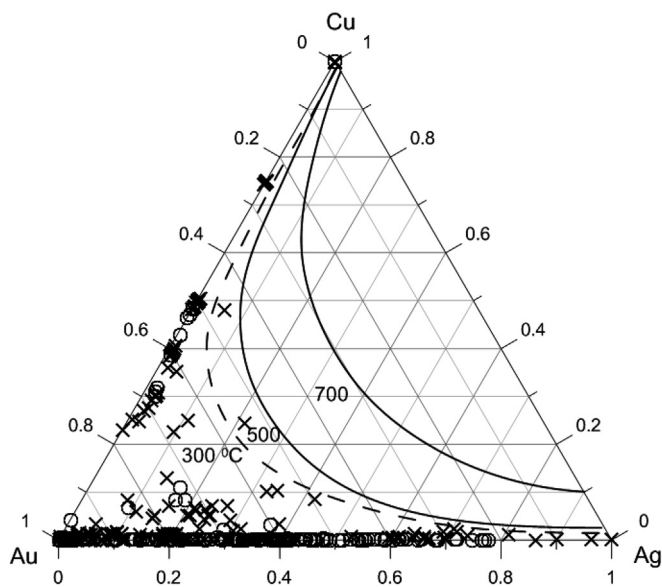
Distribution of components from the available range of ore deposits was compared to the experimental results in the system Ag–Cu–Hg (Kubaschewski, 1988). The comparison showed a good agreement of natural and experimental data (Fig. 3) despite the fact that the latter were obtained only for 37 °C.

The least studied is the ternary Au–Cu–Hg system for which no data on the distribution of metals were found in literature. The diagram in Fig. 4 shows that most points are localized in the field of gold-rich compositions and close to the Au–Cu and Au–Hg sides of the triangle.

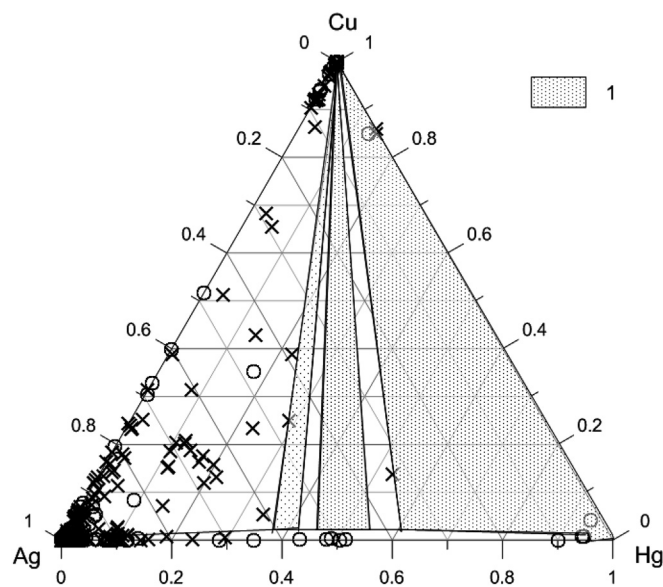
## 3. Model description

Representation of data for quaternary solid solutions in the thermodynamic model can be realized with the help of two alternative approaches. The first is the determined task of specific compositions of solid solutions that occur at the deposit studied. The advantage of this approach is the possibility for studying the formation of real mineral compositions under nonisothermic conditions. At the same time, for most ore deposits it is virtually impossible to calculate all combinations of probable metal ratios. Therefore, this form of definition of initial data in thermodynamic models often appears to be a limiting factor.

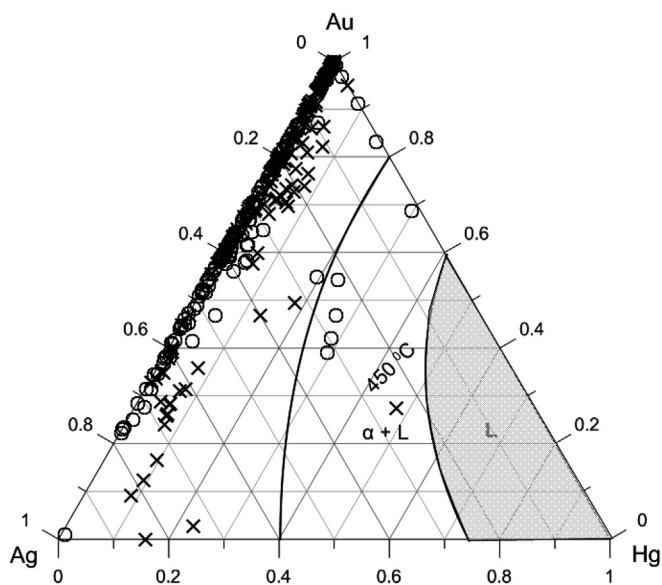
The second approach implies that the thermodynamic system includes a phase of solid solution, the end members of which are represented by four metals. Thus, stoichiometry of natural solid solutions of quaternary system is not explicitly specified in initial data. Interaction of end members is considered according to the accepted model of mixing in solid solution. Thus, composition of solid solution is not established in an explicit form but calculated as a result of minimization of Gibbs energy as a derivative of the end members entering the composition. Let us conventionally call this method “thermodynamic activity model”. Practical application of this approach was implemented in Chudnenko et al. (2015), in which on the example of the Au–Ag–Hg system in the Kyuchyus Au–Sb–Hg deposit we showed the particular features and mechanisms of formation of native gold with admixtures of mercury and silver as binary and ternary solid solutions. In this work we expanded the approach to the system of quaternary solid solutions.



**Fig. 1.** Isotherms of the miscibility gap in Cu–Ag–Au system (Prince et al., 2006). Icons represent the values from compiled database: X – primary deposits (Table 1S (Supporting Material)), circle – placer deposits (Table 2S (Supporting Material)).



**Fig. 3.** Metal ratio in Cu–Ag–Hg system from database (Tables 1S and 2S). 1 – areas of miscibility gap for 37 °C (Kubaschewski, 1988).



**Fig. 2.** Ternary diagram of Ag–Au–Hg and phase boundaries at 450 °C from (Basu et al., 1981). X – primary deposits, circle – placer deposits from database (Tables 1S and 2S). L is liquid,  $\alpha$  is solid solution.

In the discussed examples of applied models we showed the specific features of application of both approaches.

### 3.1. Thermodynamic properties of solid solutions in the Au–Ag–Cu–Hg system

Natural Au–Ag–Cu–Hg alloys are presented in the form of ordered and disordered solutions. Disordered solid solution can be in general represented by fcc structure with composition continuously varying in rather wide ranges. The composition of ordered solid solutions is not a strictly fixed metal ratio either (Cao et al., 2007; Xie et al., 2014a, b; 2015). However as a first approximation in this work let us consider that in the Au–Cu system the

intermetallics are  $\text{AuCu}_3$ ,  $\text{AuCu}$  and  $\text{Au}_3\text{Cu}$ . We did not study other stable crystallographic phases in this work.

#### 3.1.1. Disordered solid solutions

Complete estimation of standard thermodynamic functions of the quaternary system Au–Ag–Cu–Hg takes into account the interaction parameters of binary, ternary and quaternary systems. At present we do not have any reliable data on all ternary and quaternary systems and for this reason our study is restricted to a simple model taking account only of binary interactions. Preliminary performed analysis (Figs. 1–4) shows that at most ore deposits it is binary ratios that are mainly responsible for the composition and properties of quaternary solid solution.

The quaternary system Au–Ag–Cu–Hg includes 6 binary systems: Ag–Cu, Au–Cu, Cu–Hg, Au–Hg, Ag–Hg and Au–Ag. A survey of phase equilibria and estimation of standard thermodynamic functions of liquid and solid phases in the systems Ag–Hg and Cu–Hg were made in Liu et al. (2012). Data from White et al. (1957) were borrowed to calculate the standard thermodynamic properties of Ag–Au continuous solid solution (Pal'yanova et al., 2005). The detailed summary of thermodynamic data for Au–Hg, Ag–Cu and Au–Cu solid solutions, including molar thermodynamic properties (standard thermodynamic potentials and heat capacity equation), was made in (Chudnenko, Pal'yanova, 2013a, b).

Thermodynamic parameters of quaternary solid solutions in the system Au–Ag–Cu–Hg were calculated using the Guggenheim theory which suggests that the molar excess Gibbs energy of mixing of a binary solution may be represented by the polynomial expression (Guggenheim, 1952).

The Gibbs energy of one mole of solid solution at pressure 1 bar and temperature  $T$  K was calculated by equation:

$$G_T^0(x) = \sum_{i=1}^4 x_i (G_i^0 + G_i^{\text{mix}}) \quad (1)$$

where  $x_i$  is the atomic fractions of  $i$ -component in the solution,  $\sum_{i=1}^4 x_i = 1$ ;  $G_T^0(x)$  is the standard Gibbs energy of solid solution;  $G_i^0$  is the standard values of Gibbs energy end-member of solid solution. Energy of mixing of  $i$  component in the solution

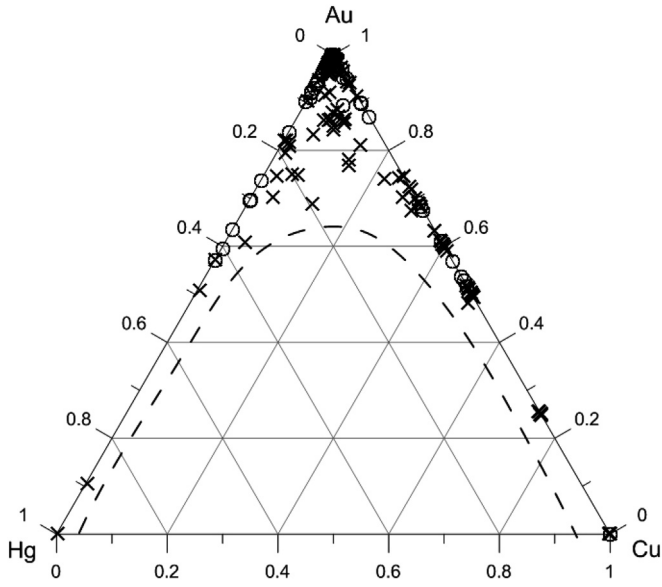


Fig. 4. Metal ratio in Cu–Au–Hg system from database (Tables 1S and 2S). The dashed line indicates the miscibility gap for typical natural systems.

$G_i^{mix} = RT \ln x_i + G_i^{ex}$  is the sum of the terms of assessing the contribution of ideal mixing ( $RT \ln x_i$ ) and deviations from the ideal in the form of the partial excess Gibbs energy ( $G_i^{ex}$ ).

The excess Gibbs energy of mixing of binary solid solution was determined using the formalism of Redlich–Kister energy (Redlich and Kister, 1948):

$$G^{ex} = \sum_i \sum_{j>i} x_i x_j \sum_{k=0}^m {}^k L_{ij} (x_i - x_j)^k \quad (2)$$

where  ${}^k L$  is the parameters of polynomial approximant;  $m$  is the degree of polynomial. In the calculations the use of the three-member Redlich–Kister polynomial was considered to be sufficient ( $m = 2$ ). Then  ${}^0 L$  is the regular solution parameter,  ${}^1 L$  is the subregular solution parameter and  ${}^2 L$  is the “subsubregular” solution parameter (Hillert, 2008). The values of parameters are given in Table 5.

The partial excess Gibbs energy of component in the quaternary subregular solutions was estimated by the equation:

$$G_i^{ex} = G^{ex} + (1 - x_i) \frac{\partial G^{ex}}{\partial x_i} - \sum_{j \neq i} x_j \frac{\partial G^{ex}}{\partial x_j} \quad (7)$$

where

$$\frac{\partial G^{ex}}{\partial x_i} = \sum_{j \neq i} x_i x_j \left[ \sum_{k=1}^2 k \cdot {}^k L_{ij} (x_i - x_j)^{k-1} \right] + \sum_{j \neq i} z x_j \left[ \sum_{k=0}^2 {}^k L_{ij} (x_i - x_j)^k \right],$$

$z = 1$  ( $i < j$ ) or  $z = -1$  ( $i > j$ ).

Activity of  $i$ -component in solid solution:

$$a_i = x_i e^{G_i^{ex}/RT} \quad (8)$$

Standard thermodynamic properties of the Au–Ag–Cu–Hg system are reported in Table 6. Values of  $\Delta_f G^0$ ,  $S^0$ ,  $V^0$ ,  $C_p$  were determined by the procedure described in (Chudnenko, Pal’yanova, 2013a, b). Thermodynamic properties were calculated for ratios Au:Ag:Hg:Cu established from data on specific ore deposits but not hypothetical compositions lying in the field of stable solid solutions.

### 3.1.2. Ordered solid solutions

Among all ordered compounds in the system Au–Ag–Cu–Hg the best studied are Au–Cu intermetallics (Okamoto et al., 1987; Prince et al., 2006; Cao et al., 2007). The studies are mainly connected with the physical properties of the system, peculiarities of order–disorder transition and parameters of crystal lattice. Standard thermodynamic properties ( $\Delta_f G^0$ ,  $S^0$ ,  $C_p$ ), necessary for performing thermodynamic modeling are reported only for AuCu<sub>3</sub> and AuCu in the database of H. Yokokawa (1988) on the basis of experiments conducted by Hultgren et al. (1973).

To calculate the thermodynamic properties of intermetallic compounds in the system Au–Cu in this work, we used the dependencies of Gibbs energy of mixing  $G_m$  for AuCu<sub>3</sub> (Xie et al., 2014a), AuCu (Xie et al., 2014b) and Au<sub>3</sub>Cu (Xie et al., 2015). The calculation procedure is described in (Chudnenko and Pal’yanova, 2013a, b). Calculated data are provided in Table 6.

### 3.2. Software and thermodynamic dataset for modeling

As the tool for studying physicochemical processes of the formation of native gold we used the universal software complex “Selektor-C” in which the method of thermodynamic modeling on the basis of the approach of convex programming is realized (Karpov et al., 1997; Chudnenko, 2010). Earlier we used the “Selektor-C” software to study the ore formation of gold–silver ormagmatic systems and associated deposits in the central part of the Okhotsk–Chukchi volcanic belt (Karpov et al., 2001) and the formation of mercuric gold at Kyuchyus Au–Sb–Hg deposit (Chudnenko et al., 2015).

The simulations were carried out for a 10-element chemical system C–Na–S–Cl–Cu–Ag–Au–Hg–H–O at temperatures 25–300 °C and pressures 1–250 bars. The calculation of

Table 5  
Redlich–Kister parameters for binary solid solution.

Binary system	System parameters, J/mol	Reference
Ag–Au	${}^0 L = -18618.8 + 5.753T$ ${}^1 L = 1673.6$	(Chudnenko and Pal’yanova, 2013a)
Ag–Cu	${}^0 L = 36772.58 - 11.02847 T$ ${}^1 L = -4612.43 + 0.28869 T$	(Dinsdale et al., 2008)
Au–Cu	${}^0 L = -28000 + 78.8T - 10T \ln(T)$ ${}^1 L = 6000$	(Sundman et al., 1998)
Au–Hg	${}^0 L = 1500 + 4.05T$ ${}^1 L = -7499.99 + 2.15T$	(Chudnenko and Pal’yanova, 2013b)
Ag–Hg	${}^0 L = -16000 + 13.9T$ ${}^1 L = -18622.9$	(Liu et al., 2012)
Cu–Hg	${}^0 L = 82000 - 15T$ ${}^1 L = -20000 - 20T$ ${}^2 L = -34T$	(Liu et al., 2012)

**Table 6**

Standard thermodynamic properties of the Au–Ag–Cu–Hg native solid solutions and intermetallic compounds.

Components	Ref.	$\Delta_f G^0$ , J/mol	$S^0$ , J/mol/K	$V^0$ , cm <sup>3</sup> /mol	$C_p = a_1 + a_2 T^{-2} + a_3 T^{-3} + a_4 T^{-0.5}$ , J/mol/K			
					$a_1$	$a_2 \cdot 10^5$	$a_3 \cdot 10^7$	$a_4 \cdot 10$
<i>Solid solution</i>								
Au <sub>0.951</sub> Ag <sub>0.001</sub> Cu <sub>0.042</sub> Hg <sub>0.006</sub>	1	–1198	48.360	10.108	51.4870	48.4845	–87.0200	–83.4644
Au <sub>0.915</sub> Ag <sub>0.051</sub> Cu <sub>0.033</sub> Hg <sub>0.001</sub>	2	–2030	49.110	10.119	51.4817	47.9167	–85.5075	–83.4369
Au <sub>0.907</sub> Ag <sub>0.002</sub> Cu <sub>0.004</sub> Hg <sub>0.087</sub>	3	–1122	52.173	10.540	50.5673	47.3871	–84.8424	–81.5085
Au <sub>0.861</sub> Ag <sub>0.133</sub> Cu <sub>0.002</sub> Hg <sub>0.004</sub>	4	–2904	49.802	10.232	51.5364	47.8135	–84.7366	–84.1999
Au <sub>0.813</sub> Ag <sub>0.089</sub> Cu <sub>0.066</sub> Hg <sub>0.032</sub>	3	–3465	51.467	10.139	51.5876	47.1395	–83.7175	–82.7209
Au <sub>0.775</sub> Ag <sub>0.104</sub> Cu <sub>0.056</sub> Hg <sub>0.065</sub>	2	–3648	53.203	10.299	51.3232	46.668	–82.5486	–82.0701
Au <sub>0.714</sub> Ag <sub>0.153</sub> Cu <sub>0.067</sub> Hg <sub>0.066</sub>	2	–4324	53.621	10.272	51.5435	46.4942	–81.9631	–82.4054
Au <sub>0.674</sub> Ag <sub>0.239</sub> Cu <sub>0.049</sub> Hg <sub>0.038</sub>	2	–5031	52.577	10.224	51.9164	46.6221	–81.7315	–83.7563
Au <sub>0.664</sub> Ag <sub>0.220</sub> Cu <sub>0.059</sub> Hg <sub>0.057</sub>	2	–4935	53.464	10.265	51.7564	46.3447	–81.2497	–83.07
Au <sub>0.625</sub> Ag <sub>0.372</sub> Cu <sub>0.001</sub> Hg <sub>0.002</sub>	5	–5535	49.998	10.241	52.3977	46.9146	–81.5072	–85.8783
Au <sub>0.541</sub> Ag <sub>0.308</sub> Cu <sub>0.095</sub> Hg <sub>0.056</sub>	2	–5342	53.622	10.155	52.1457	45.8016	–79.7376	–83.4562
Au <sub>0.453</sub> Ag <sub>0.059</sub> Cu <sub>0.472</sub> Hg <sub>0.016</sub>	2	–5949	46.558	8.816	52.1096	43.2291	–76.6918	–78.3582
Au <sub>0.433</sub> Ag <sub>0.370</sub> Cu <sub>0.075</sub> Hg <sub>0.122</sub>	2	–5349	56.126	10.476	51.8473	45.133	–77.8766	–82.7818
Au <sub>0.419</sub> Ag <sub>0.296</sub> Cu <sub>0.002</sub> Hg <sub>0.283</sub>	6	–5536	60.749	11.322	50.3073	43.774	–74.9496	–78.9972
Au <sub>0.309</sub> Ag <sub>0.624</sub> Cu <sub>0.002</sub> Hg <sub>0.065</sub>	7	–6307	51.513	10.496	52.875	45.0896	–76.161	–86.0879
Au <sub>0.281</sub> Ag <sub>0.657</sub> Cu <sub>0.001</sub> Hg <sub>0.061</sub>	7	–6125	51.007	10.486	53.0028	44.9565	–75.6869	–86.3483
Au <sub>0.091</sub> Ag <sub>0.821</sub> Cu <sub>0.001</sub> Hg <sub>0.087</sub>	7	–4613	49.429	10.596	53.4033	43.931	–72.5623	–86.8029
Au <sub>0.027</sub> Ag <sub>0.742</sub> Cu <sub>0.001</sub> Hg <sub>0.23</sub>	7	–5593	53.365	11.145	52.4844	43.7281	–72.5688	–84.2556
<i>Intermetallics</i>								
AuCu <sub>3</sub>		–28928	150.312	31.554	–191.4	–612.625	692.57	1151.705
AuCu		–17589	80.255	17.328	239.984	337.313	–617.491	–585.992
Au <sub>3</sub> Cu		–23824	195.608	37.758	846.74	2949.21	–6675.72	–3027.03

1 – Meisser and Brugger (2000), 2 – Kucha and Raith (2009), 3 – Naumov and Naumova (2014), 4 – Higgins (2012), 5 – Dumula and Mortensen (2002), 6 – Barkov (2009), 7 – Sammelin et al. (2011).

thermodynamic relationships for aqueous solution components was performed using the modified equation HKF (Tanger and Helgeson, 1988). The simulated multisystem involved 42 possible minerals, aqueous solution with 66 simple and complex ions and molecules, and gas solution consisting of 12 components. The list of the minerals, aqueous and gaseous species in the model is presented in Table 3S (Supporting Material). Thermodynamic data obtained from database of “Selektor-C” software and reference data are given in Chudnenko et al. (2015). In the applied examples we also used thermodynamic data on the quaternary solid solution Au–Ag–Cu–Hg (this study), binary and ternary solid solutions (Chudnenko and Palyanova, 2013a, b).

#### 4. Results and discussion

Let us demonstrate some features of formation of different Au–Ag–Cu–Hg alloys on the basis of models developed using the procedure described in this paper. These examples do not claim to solve global tasks of determination of ore genesis problems or to represent the complete picture of the occurrence of physicochemical processes at this or that deposit. This is the subject of independent researches with the involvement of the whole mass of geologic, petrologic and geochemical data. Here we only touch upon some aspects of this general problem with the aim to estimate the physicochemical parameters that are of interest for studying ore formation processes.

The main problem is to determine the effect of temperature and composition of ore-forming fluid, which is equilibrated with the quaternary solid solutions that are similar to natural solutions at different types of deposits. Desborough et al. (1970), Boyle (1979), Petrovskaya (1993) and other authors attribute compositional variations in natural alloys of Au, Ag, Cu, Hg etc. to the conditions of ore formation. The effect of physicochemical conditions on silver concentration in native gold, considering formation of solid solution  $Ag_xAu_{1-x}$  ( $0 \leq x \leq 1$ ), was reported in (Gammons, Williams-Jones, 1995; Palyanova, 2008; Liang and Hoshino, 2015). The amount of silver in native gold may be the characteristics that

depends on temperature, pH, redox conditions, chloride, and sulfide concentrations and evolution of ore solution in the process of hydrothermal deposit formation. It is worth noting that establishment of the main physicochemical parameters of ore-forming fluids is in many cases involved with particular difficulties as there is no possibility for attracting direct analysis of data on natural objects.

The calculated thermodynamic properties of the Au–Ag–Cu–Hg quaternary system with the frames of fcc disordered solid solutions and Au–Cu intermetallics allow one to carry

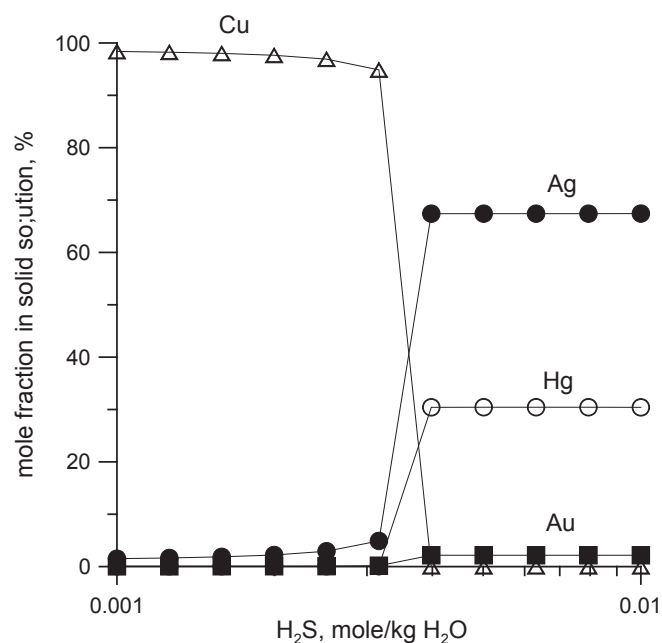


Fig. 5. Formation of solid solution depending on H<sub>2</sub>S content in fluid (molality Hg  $10^{-6} - 10^{-5}$ ). T = 200 °C.



out model calculations and to reveal the peculiarities of formation of native gold with different contents of silver, copper and mercury at different  $T,P,X$ -parameters. In the ore deposits chosen for modeling no formation of ordered solid solutions of other metals was revealed. Therefore, it is most likely that such simplification of models will not influence the obtained results.

As the first example let us consider the Aitik Cu–Au–Ag porphyry deposit. It is Sweden's largest copper mine and one of Europe's most important copper producers (Wanhainen et al., 2003). It is noteworthy that mercury is absent among major and trace element analyses of representative samples from the Aitik rock types (Wanhainen et al., 2012) and in fluid inclusions (Smith et al., 2013). The more interesting was the detection of Hg in the gold grains of the strongly metamorphosed Aitik ore of post-metamorphic origin (Sammelin et al., 2011). Amalgams in the Aitik probably formed relatively late in the mineralizing process.

Initial composition of model fluid was specified on the basis of evaluation data on the salinity reconstructed from fluid inclusions (Smith et al., 2013) and assumption on fluid reduction in front zones of metasomatism (in mol/kg H<sub>2</sub>O): H<sub>2</sub>S = 0.001–0.01, CO<sub>2</sub> = 0.001, NaCl = 0.5, NaOH = 0.01. Ore components were chosen base on the data of fluid inclusions (ppm): Cu = 5182; Ag = 102;

Au = 6 (Smith et al., 2013). The probable mercury content was to be estimated as such data were not found in the above-cited works. Modeling was conducted at  $T = 200$  °C.

Since, in spite of the high Cu content at deposits, solid solutions Au–Ag–Cu–Hg contained minor or no copper (Table 1S (Supporting Material)), we first modeled a sufficient initial amount of H<sub>2</sub>S in fluid, which helped explain this regularity (Fig. 5). At excess content of hydrogen sulfide (H<sub>2</sub>S > 0.004 mol/kg H<sub>2</sub>O) copper in the model is realized mainly in dissolved forms to 1.6 mmol/(kg H<sub>2</sub>O) (mainly as ions CuHS<sup>0</sup>, Cu(HS)<sup>2-</sup>) and as chalcocite (Cu<sub>2</sub>S). Thus, copper content in solid solutions Au–Ag–Cu–Hg is less than 0.1 mol fraction.

To compare different approaches in the thermodynamic modeling of ore formation from post-metamorphic fluid, we analyzed a number of solid solution models: binary, ternary, and quaternary “thermodynamic activity models”, when the composition of solid solution is determined from the calculation of equilibrium state of the system, and the model of fixed compositions of solid solutions from Table 6 for a particular deposit is Au<sub>0.281</sub>Ag<sub>0.657</sub>Cu<sub>0.001</sub>Hg<sub>0.061</sub>, Au<sub>0.091</sub>Ag<sub>0.821</sub>Cu<sub>0.001</sub>Hg<sub>0.087</sub>, and Au<sub>0.027</sub>Ag<sub>0.742</sub>Cu<sub>0.001</sub>Hg<sub>0.23</sub>.

In the model of binary solid solutions (Fig. 6a) the solid solutions

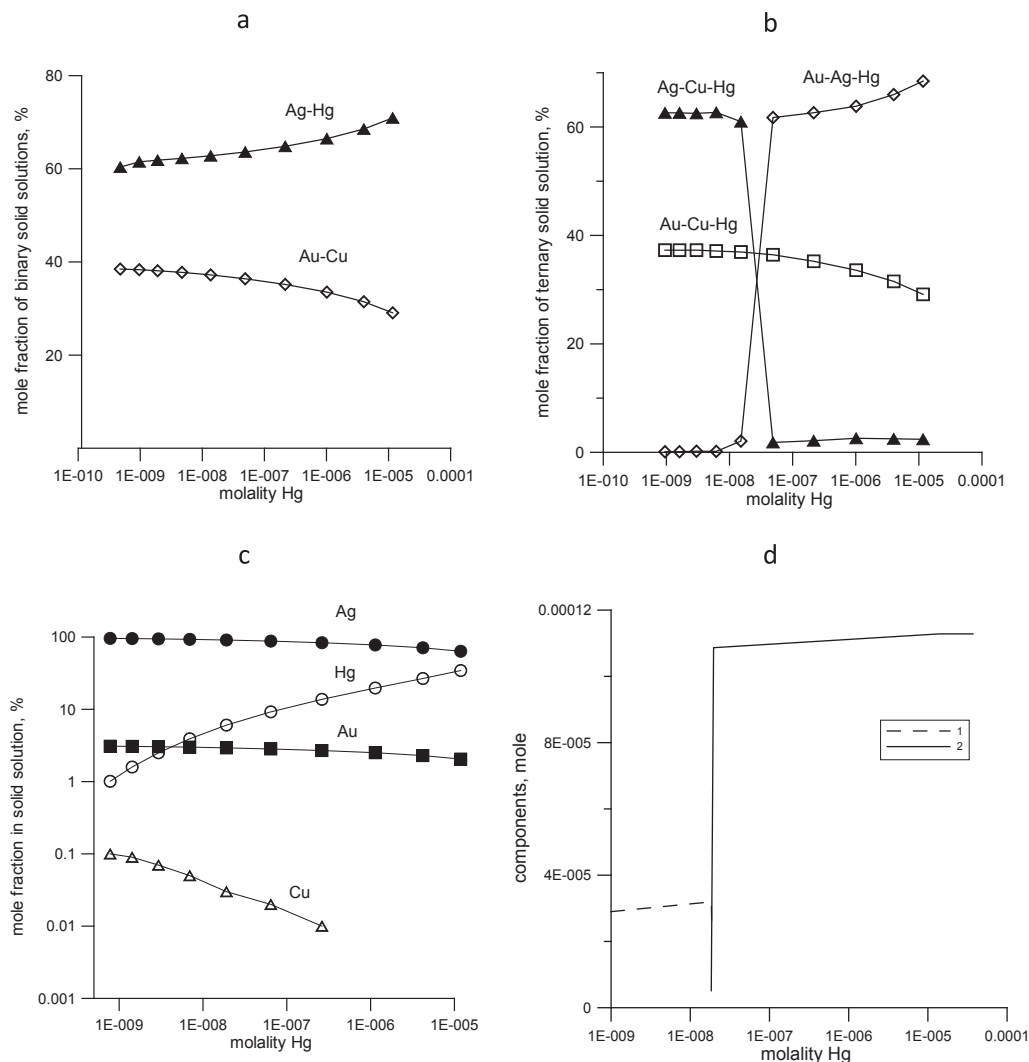


Fig. 6. Calculated composition of solid solutions depending on Hg content in post-metamorphic fluid at the Aitik deposit. a–c – “activity model”: a – binary solid solutions; b – ternary solid solutions; c – quaternary solid solutions; d – solid solutions of fixed composition (1 – Au<sub>0.091</sub>Ag<sub>0.821</sub>Cu<sub>0.001</sub>Hg<sub>0.087</sub>; 2 – Au<sub>0.027</sub>Ag<sub>0.742</sub>Cu<sub>0.001</sub>Hg<sub>0.23</sub>).

Ag–Hg and Au–Cu are present in the whole range of mercury content in the fluid. As all solid mercury is realized in the binary solid solution Ag–Hg, its fraction grows with increasing of mercury content in the system, reaching 0.7 mol fraction at  $10^{-5}$  Hg molality. The composition of Au–Cu solid solution remains constant and equals  $\text{Cu}_{0.95}\text{Au}_{0.05}$  because the content of gold and copper in the calculations does not change.

In the model of ternary solid solutions (Fig. 6b) mercury enters into the composition of three solid solutions: Ag–Cu–Hg, Au–Ag–Hg and Au–Cu–Hg. In spite of the opposite tendency of quantitative change in the model of Ag–Cu–Hg and Au–Ag–Hg, molar fraction of mercury increases in both solid solutions. However, inversion of their relationship in the system takes place at  $5 \cdot 10^{-8}$  Hg molality and, therefore, the main ternary solid solution in which mercury accumulates is Au–Ag–Hg. In Au–Cu–Hg mercury content tends to zero, turning this solid solution into binary Au–Cu.

The model of a quaternary solid solutions (Fig. 6c) presents compactly summarized information on natural gold. As a result of performed modeling we obtained the composition of solid solution  $\text{Ag}_{0.635}\text{Hg}_{0.344}\text{Au}_{0.021}$ , which is similar to gold grains from [Sammelin et al. \(2011\)](#). Suffice mercury content in the fluid is  $10^{-6} - 10^{-5}$  mol/kg  $\text{H}_2\text{O}$ . With this assumption, the data on the occurrence of Hg in Au–Ag mineral associations can be also obtained from the models with binary and ternary solid solutions, but it is impossible exactly to reproduce the compositions of natural solid solutions because Cu also enters other Au- or Ag-bearing phases.

The model of fixed compositions yields results far more distant from reality (Fig. 6d). Although the threshold of transition to the formation of solid solution with a high Hg content differs slightly from previous models, the rigid model (Fig. 6d) does not allow obtaining gradual change in solid solution composition as the number of fixed solid solutions in the model is limited. Therefore it is impossible to estimate the Hg molality values, at which formation of amalgams takes place at the Aitik. It is understandable by intuition that, if we introduce a rather large amount of solid solutions of fixed composition into the model, in which the Ag:Au:Hg ratio changes slowly step-by-step, we can obtain the same results as in the “activity model” (Fig. 6c) but this approach requires consideration of all probable combinations of component ratios in solid solution and for this reason it is difficult to realize it in practice.

Another example is the Cu–Au–Ag Wheaton Creek deposit (Canada). Results to date indicate that the source of the placer gold has not been located. One interpretation of the data may indicate that the gold-bearing rock has been completely glaciated and eroded/weathered, leaving essentially the roots of the mineralized system. Representative ores from the Wheaton Creek deposit (ppm): Au = 0.0005–3.5; Ag = 0.1–7; Cu = 0.1–965; Hg = 0.01–0.34 ([Downing, 2013](#)). The compositions of the principal phases within gold particles from deposit are represented mainly by AuCu,  $\text{Au}_3\text{Cu}$  and  $\text{Au}_2\text{Cu}$  (Fig. 7).

The aim of thermodynamic modeling was to answer the question: is the phase ratio of intermetallic compounds at the Wheaton Creek deposit, when the number of samples with  $\text{Au}_3\text{Cu}$  and AuCu clearly dominates over the number of samples with  $\text{AuCu}_3$ , regular or incidental? We modeled two scenarios of formation of the Au–Cu alloy compositions in placer deposits: endogenous gold from native source and further partial dissolution in surface conditions with formation of secondary gold. The calculations, along with the quaternary solid solution phases, included intermetallics  $\text{AuCu}_3$ , AuCu and  $\text{Au}_3\text{Cu}$  (Table 6).

Fluid composition in the first scenario was specified on the basis of general parameters of endogenous solutions (mol/kg  $\text{H}_2\text{O}$ ):  $\text{H}_2\text{S} = 0.00001$ ,  $\text{CO}_2 = 0.001$ ,  $\text{NaCl} = 0.5$ ,  $\text{NaOH} = 0.01$ . The amount

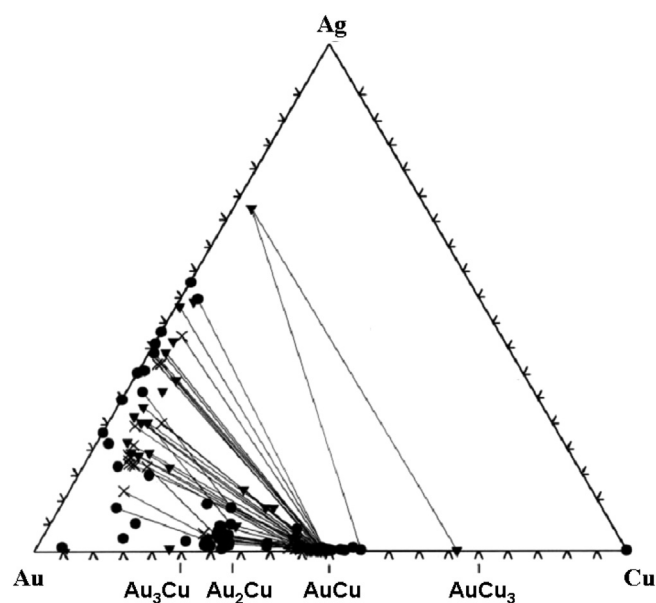


Fig. 7. Data for the compositions of principal phases within gold particles from Wheaton Creek. X – exsolved phase, inverted triangle – blebby phase, bold point – massive phase. The tie-lines of joined phases considered to be in equilibrium ([Knight and Leitch, 2001](#)).

of Au was specified as 3.5 ppm, whereas Ag and Hg, as average values from [Downing \(2013\)](#). Since the amount of Cu ranges widely, the calculations were performed in the range of Cu = 0.1–965 ppm. Modeling temperature was 130 °C according to [Knipe and Fleet \(1997\)](#), in which this temperature is assumed to correspond to the formation of natural  $\text{Au}_3\text{Cu}$ .

Results of calculation are shown in Fig. 8. Intermetallic compounds form according to the ratio Au:Cu, though there are some differences from the classic phase diagram in the system Au–Cu ([Cao et al., 2007](#)). This is due to the fact that the system in addition to Au and Cu also contains Ag and Hg, which enter into the phase of quaternary solid solution. Solid solution Au–Ag–Cu–Hg dominates both at low Cu content in the system ( $\text{Au}/\text{Cu} < 0.1$ ) and at high Cu concentration ( $\text{Au}/\text{Cu} > 10$ ). Moreover, its amount slightly increases in the intervals of transition between the stability regions of intermetallics.

In the second scenario we took Au/Cu ratios obtained at  $T = 130$  °C, which correspond to intermetallic compounds:  $\text{Au}_3\text{Cu}$ , AuCu and  $\text{AuCu}_3$ . The solution is represented by nonmineralized rain water: 1 kg  $\text{H}_2\text{O} + 0.0000023 \text{ mH}_2\text{CO}_3 + 0.00001368 \text{ m CO}_2 + 0.00032 \text{ m O}_2$  (25 °C, 1 bar), pH = 5.6, Eh = 0.89 ([Karpov et al., 2001](#)). The calculations were carried out at a fixed number of solid phases (0.4 g for  $\text{Au}_3\text{Cu}$ , 0.5 g for AuCu and 0.75 for  $\text{AuCu}_3$ ) and change in the amount of rain water of 0.01–50 kg (Fig. 9).

Oxidizing processes begin to influence  $\text{Au}_3\text{Cu}$  (Fig. 9a) from the ratio water/rock = 250. By that moment the accompanying quantity of AuCu consistently decreasing, disappears completely. Simultaneously, with a decrease in the fraction of  $\text{Au}_3\text{Cu}$ , the fraction of disorder solid solution Au–Ag–Cu–Hg increases. Under the impact of 4 kg water solution, most of gold goes into aqueous solution and only tenorite remains in solid phase.

A similar picture was observed upon decomposition of AuCu (Fig. 9b). The first to vanish here is the accompanying intermetallic  $\text{AuCu}_3$  at water/rock = 200. Upon the destruction of  $\text{AuCu}$  the first to form is secondary  $\text{Au}_3\text{Cu}$  and thereafter a disorder solid solution. Further increase in the amount of aqueous solution leads to complete dissolution of ore components, ruling out Cu. Transformation

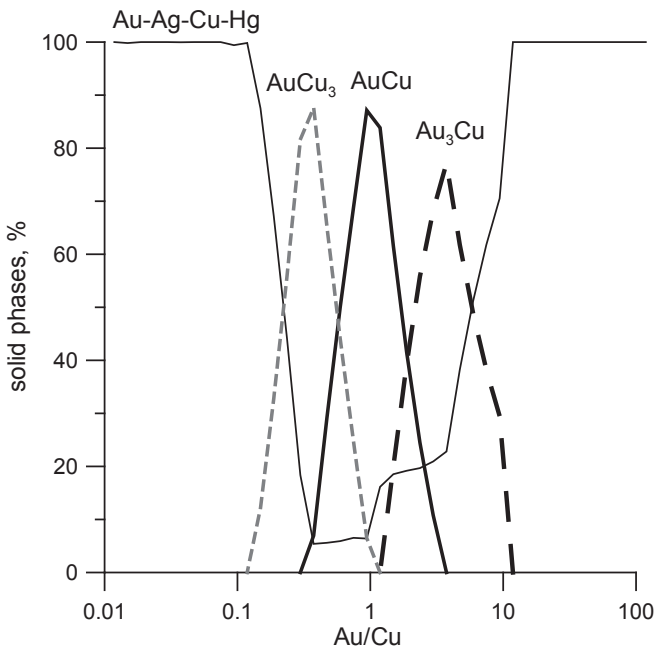


Fig. 8. Compositions of equilibrium phases in the model for the Wheaton Creek deposit. T = 130 °C.

of AuCu<sub>3</sub> (Fig. 9c) also follows the described order but here one stage with the formation of secondary AuCu is added.

Therefore, decomposition of intermetallic compounds under the influence of hypergene processes at the Wheaton Creek deposit takes place according to the following scheme: AuCu<sub>3</sub> → AuCu → Au<sub>3</sub>Cu → disordered solid solution → Cu oxides. This regularity of formation of secondary gold alloys is supported by the ratio of observed intermetallics (Knight and Leitch, 2001) and can be regarded as one of working hypotheses of occurrence of hypergene transformations at placer deposits.

### 5. Conclusions

Ore deposits containing natural alloys of Au, Ag, Cu and Hg, which cannot be referred to the category of rare alloys, are of lesser occurrence than deposits with natural alloys of Au–Ag, Au–Ag–Cu or Au–Ag–Hg. This is due both to the quantitative amount of components in ores and to the regularities and restrictions of physicochemical conditions that are not always simultaneously easily realizable at various deposits.

In this work an attempt was made to analyze the probability of generation of such a type of solid solutions within the frames of a thermodynamic approach. We calculated thermodynamic properties of some natural solid solutions from different deposits and Au<sub>3</sub>Cu, AuCu and AuCu<sub>3</sub> intermetallics. For disordered quaternary solid solutions we propose equations for calculation of excess Gibbs

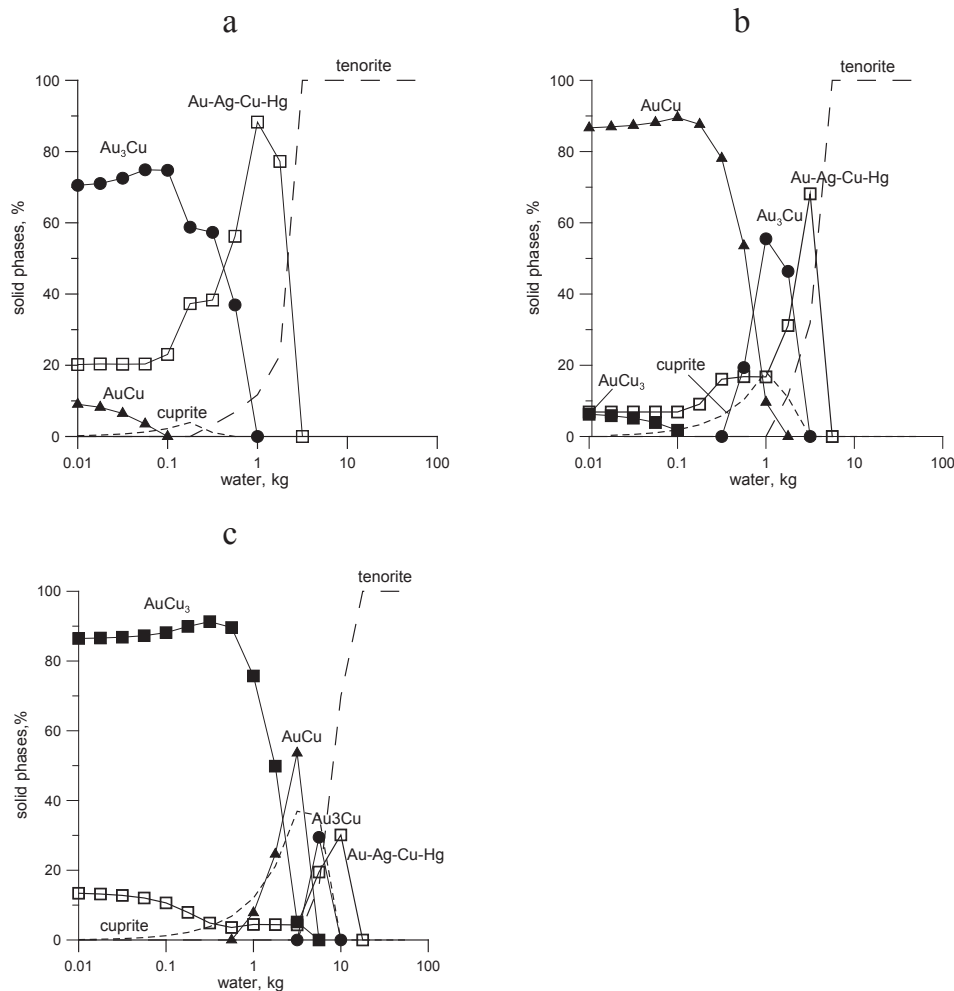


Fig. 9. Transformation of intermetallic compounds under hypergene conditions in the model for the Wheaton Creek deposit. a – Au<sub>3</sub>Cu, b – AuCu, c – AuCu<sub>3</sub>.

energy functions of Au, Ag, Cu, and Hg in solid solutions, which were used for developing a block of calculations of component activities in the “Selektor-C” software. This program was used for modeling equilibrium conditions of formation of natural alloys of Au, Ag, Cu and Hg. Since the problems associated with the deposits of native gold and silver are of the greatest interest, we chose typical representatives of Au–Ag–Cu–Hg ore occurrences as deposits for study. Ore formation scenarios were modeled for two deposits. In the first model we studied the effect of initial Hg and H<sub>2</sub>S concentrations in the formation of quaternary solid solutions in hydrothermal conditions at the Aitik Cu–Au–Ag porphyry deposit (Sweden). The modeling showed that for the formation of solid solution of Ag<sub>0.635</sub>Hg<sub>0.344</sub>Au<sub>0.021</sub>, which is similar to gold grains from the Aitik deposit, the suffice mercury content in the fluid is 10<sup>-6</sup> – 10<sup>-5</sup> molality. In the second model we analyzed the formation of intermetallic compounds under the effect of endogenic and hypergene processes at the Wheaton Creek placer deposit (Canada). This assertion is in no case a strict rule but it only reflects a particular trend that is realized in favorable conditions. Some of perturbing factors are specific ratios of other ore components, *P*, *T* conditions differing from those discussed above, presence of superimposed processes, kinetics, etc. At the same time, the approach described in this work can be used as an additional tool in the analysis of the genesis of gold deposits and be efficient in the estimation of formation of solid solutions that are in many cases the main carriers of ore components.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2015.12.005>.

## References

- ASM handbook, v.3: Alloy phase diagrams, 1992.
- Barkov, A.Y., Nixon, G.T., Levson, V.M., Martin, R.F., 2009. A cryptically zoned amalgam (Au<sub>1.5–1.9</sub>Ag<sub>1.1–1.4</sub>)<sub>2.8–3.0</sub>Hg<sub>1.0–1.2</sub> from a placer deposit in the Tulameen – Similkameen river system British Columbia, Canada: natural or man-made? *Can. Mineral.* 47, 433–440.
- Basu, K., Bortnikov, N., Mookherjee, A., Mozgova, N., Tsepin, A.I., 1981. Rare minerals from Rajpura-Dariba, Rajasthan, India II. Intermetallic compound Ag<sub>74.2</sub>Au<sub>16.4</sub>Hg<sub>9.4</sub>. *Neues Jahrbuch Mineralogie Abhandlungen* 141, 217–223.
- Bond, D.P.G., Chapman, R.J., 2007. Evaluation of the origins of gold hosted by the conglomerates of the Indian River formation, Yukon, using a combined sedimentological and mineralogical approach. In: Emond, D.S., Lewis, L.L., Weston, L.H. (Eds.), *Yukon Exploration and Geology 2006*. Yukon Geological Survey, pp. 93–103.
- Bonev, I.K., Kerestedjian, T., Atanassova, R., Andrew, C.J., 2002. Morphogenesis and composition of native gold in the Chelopech volcanic-hosted Au–Cu epithermal deposit, Srednogie zone, Bulgaria. *Miner. Deposita* 37, 614–629.
- Boyle, R.W., 1979. *The Geochemistry of Gold and its Deposits*. Geol. Surv. Canada, Ottawa.
- Cao, W., Chang, Y.A., Zhu, J., Chen, S., Oates, W.A., 2007. Thermodynamic modeling of the Cu–Ag–Au system using the cluster/site approximation. *Intermetallics* 15, 1438–1446.
- Chang, Y.A., Goldberg, D., Neumann, J.P., 1977. Phase diagrams and thermodynamic properties of ternary copper–silver systems. *J. Phys. Chem. Ref. Data* 6 (3), 621–674.
- Chapman, R.J., Mortensen, J.K., LeBarge, W.P., 2011. Styles of lode gold mineralization contributing to the placers of the Indian River and Black Hills Creek, Yukon Territory, Canada as deduced from microchemical characterization of placer gold grains. *Miner. Deposita* 46, 881–903.
- Chudnenko, K.V., 2010. *Thermodynamic Modeling in Geochemistry: Theory, Algorithms, Software, Applications*. Academic Publishing House Geo, Novosibirsk (in Russian).
- Chudnenko, K., Palyanova, G., 2013a. Thermodynamic properties of Ag–Au–Hg solid solutions. *Thermochim. Acta* 572, 65–70.
- Chudnenko, K., Palyanova, G., 2013b. Thermodynamic properties of Au–Hg binary solid solution. *Thermochim. Acta* 566, 175–180.
- Chudnenko, K.V., Palyanova, G.A., 2014. Thermodynamic properties of solid solutions in the Ag–Au–Cu system. *Russ. Geol. Geophys.* 55, 349–360.
- Chudnenko, K.V., Palyanova, G.A., Anisimova, G.S., Moskvitin, S.G., 2015. Physicochemical modeling of formation of Ag–Au–Hg solid solutions: Kyuchyus deposit (Yakutia, Russia) as an example. *Appl. Geochem.* 55, 138–151.
- Desborough, G.A., Raymond, W.H., Iagmin, P.J., 1970. Distribution of silver and copper in placer gold derived from the northeastern part of the Colorado Mineral Belt. *Econ. Geol.* 65, 937–944.
- Dinsdale, A.T., Watson, A., Kroupa, A., Zemanowa, A., Vrestal, J., Vidal, J., 2008. COST 531. V. 3.0 Thermodynamic Database. <http://www.univie.ac.at/cost531/>.
- Downing, B.W., 2013. Wheaton Creek Area, Northern British Columbia. Assessment Report on Drilling Program, Danika Claim Group, Vancouver.
- Downs, B., Pasero, M., Ciriotti, M., 2007. IMA Mineral List with Database of Mineral Properties. Cambridge. <http://rruff.info/ima>.
- Dumula, M.R., Mortensen, J.K., 2002. Composition of placer and lode gold as an exploration tool in the Stewart River map area, western Yukon. In: Emond, D.S., Weston, L.H., Lewis, L.L. (Eds.), *Yukon Exploration and Geology 2001*. Exploration and Geological Services Division, Yukon Region, Indian and Northern Affairs Canada, pp. 87–102.
- Gammons, C.H., Williams-Jones, A.E., 1995. Hydrothermal geochemistry of electrum: thermodynamic constraints. *Econ. Geol.* 90, 420–432.
- Guggenheim, E.A., 1952. *Mixtures: the Theory of the Equilibrium Properties of Some Simple Classes of Mixtures Solutions and Alloys*. Clarendon Press, Oxford.
- Healy, R., Petruk, W., 1990. Petrology of Au–Ag–Hg alloy and invisible gold in the Trout Lake massive sulfide deposit Flin Flon, Manitoba. *Can. Mineral.* 28, 189–206.
- Higgins, M., 2012. Placer Gold Provenance in the Black Hills Creek, West-central Yukon: Insight from Grain Morphology and Geochemistry. Degree of Bachelor of Sciences, Honours Department of Earth Sciences, Dalhousie University, Halifax, Nova Scotia.
- Hillert, M., 2008. *Phase Equilibria, Phase Diagrams and Phase Transformations*. Cambridge University Press, Cambridge.
- Hultgren, R., Desai, P.D., Hawkins, D.T., Gleiser, M., Kelley, K.K., 1973. *Selected Values of the Thermodynamic Properties of Binary Alloys*. Am. Soc. Met., Metals Park, Ohio.
- Karpov, I.K., Chudnenko, K.V., Kulik, D.A., 1997. Modeling chemical mass-transfer in geochemical processes: thermodynamic relations, conditions of equilibria and numerical algorithms. *Am. J. Sci.* 297, 767–806.
- Karpov, I.K., Chudnenko, K.V., Kravtsova, R.G., Bychinskiy, V.A., 2001. Simulation modeling of physical and chemical processes of dissolution, transport and deposition of gold in epithermal gold-silver deposits of the North-East Russia. *Geol. Geophys.* 3, 393–408.
- Knight, J., Leitch, C.H.B., 2001. Phase relations in the system Au–Cu–Ag at low temperatures, based on natural assemblages. *Can. Mineral.* 39, 889–905.
- Knipe, S.W., Fleet, M.E., 1997. Gold–copper alloy minerals from the Kerr mine, Ontario. *Can. Mineral.* 35, 573–586.
- Kubaschewski, O., 1988. Ag–Cu–Hg ternary phase diagram evaluation. In: Effenberg, G. (Ed.), *MSI Eureka*. MSI, Materials Science International Services GmbH, Stuttgart. Document ID: 10.16021.1.5.
- Kucha, H., Raith, J.G., 2009. Gold-oxysulphides in copper deposits of the Greywacke Zone, Austria: a mineral chemical and infrared fluid inclusion study. *Ore Geol. Rev.* 35 (1), 87–100.
- Kudryavtseva, A.I., Kudryavtsev, V.I., 2003. The presence of copper gold and silver gold in noble-metal mineralization of the South Tuva ultrabasic complex. In: Lebedev, V.I. (Ed.), *The State and Exploration of the Natural Resources of Tuva and Adjacent Regions of Central Asia*. Geocology of Environment and Society. TuvIKOPR SB RAS, Kyzyl, pp. 45–48 (in Russian).
- Liang, Y., Hoshino, K., 2015. Thermodynamic calculations of Au<sub>x</sub>Ag<sub>1-x</sub> – fluid equilibria and their applications for ore-forming conditions. *Appl. Geochem.* 52, 109–117.
- Liu, Y., Wang, G., Wang, J., Chen, Y., Long, Z., 2012. Phase equilibria and thermodynamic functions for Ag–Hg and Cu–Hg binary systems. *Thermochim. Acta* 547, 83–88.
- Lyakishev, N.P. (Ed.), 1996. *State Diagrams of Binary Metal Systems*. Mashinostroenie, Moscow (in Russian).
- Marquez-Zavalia, M.F., Southam, G., Craig, J.R., Galliski, M.A., 2004. Morphological and chemical study of placer gold from the San Luis Range, Argentina. *Can. Mineral.* 42, 169–182.
- Meisser, N., Brugger, J., 2000. Alluvial native gold, tetraauricupride and AuSn<sub>2</sub> from Western Switzerland. *Schweiz. Mineral. Petrogr. Mitt* 80, 291–298.
- Morales Ruano, S., Carrillo Rosua, F.J., Fenoll Hach-Ali, P., De La Fuente Chacon, F., Contreras Lopez, E., 2000. Epithermal Cu–Au mineralization in the Palai–Islica deposit, Almeria, southeastern Spain: fluid-inclusion evidence for mixing of fluids as a guide to gold mineralization. *Can. Mineral.* 38, 553–565.
- Mudaliar, G.G., Richards, J.P., Eccles, D.R., 2007. Gold, Platinum and Diamond Placer Deposits in Alluvial Gravels, Whitecourt, Alberta. EUB/AGS Special Report 89.
- Murzin, V.V., Sazonov, V.N., Varlamov, D.A., Shanina, S.N., 2006. Gold mineralization in rodingites of Alpine-type ultrabasic massifs. *Litosfera* 1, 113–134 (in

- Russian).
- Naumov, V.A., Naumova, O.B., 2014. Interaction of gold with mercury in Ural technogenic dumps. *Mod. Problems Sci. Educ.* 6. <http://www.science-education.ru/pdf/2014/6/583.pdf>.
- Naumov, V.A., Kazymov, K.P., Osovetskiy, B.M., LeBarge, W., 2010. Crystallomorphology and Chemical Composition of in Placer Glacial Region of Yukon (Canada). *Bu. Perm State Univ. Geol.* 1 (9), 24–32.
- Okamoto, H., Chakrabarti, D.J., Laughlin, D.E., Massalski, T.B., 1987. The Au–Cu (Gold–Copper) system. *Bull. Alloy Phase Diagrams* 8, 454–474.
- Ozolins, V., Wolverson, C., Zunger, A., 1998. Cu–Au, Ag–Au, Cu–Ag and Ni–Au intermetallics: first-principles study of phase diagrams and structures. *Phys. Rev. B* 57 (11), 6427–6443.
- Pal'yanova, G.A., Shvarov, Y.V., Shironosova, G.P., Laptev, Y.V., 2005. Methodological approaches to the assessment of gold fineness during thermodynamic modeling of hydrothermal systems. *Geochem. Int.* 43 (12), 1247–1251.
- Palyanova, G., 2008. Physicochemical modeling of the coupled behavior of gold and silver in hydrothermal processes: gold fineness, Au/Ag ratios and their possible implications. *Chem. Geol.* 255, 399–413.
- Petrovskaya, N.V., 1993. *Gold Nuggets*. Nauka, Moscow (in Russian).
- Prince, A., Velikanova, T., Turchanin, M.A., 2006. Silver–Gold–Copper. In: Landolt-Boernstein, Numerical Data and Functional Relationships in Science and Technology (New Series). Group IV: Physical Chemistry. Ed. Martienssen, W., "Ternary Alloy Systems. Phase Diagrams, Crystallographic and Thermodynamic Data". Eds. Effenberg, G., Ilyenko, S., Germany, Berlin, Heidelberg: Springer-Verlag, 11B, 10–41.
- Redlich, O., Kister, A.T., 1948. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* 40, 248–345.
- Carrillo Rosua, F.J., Morales Ruano, S., Fenoll Hach-Ali, P., 2002. The three generations of gold in the Palai-Islica epithermal deposit, Southeastern Spain. *Can. Mineral.* 40, 1465–1481.
- Sammelin, M., Wanhainen, C., Martinsson, O., 2011. Gold mineralogy at the Aitik Cu–Au–Ag deposit, Gällivare area, northern Sweden. *GFF* 133 (1–2), 19–30.
- Shikazono, N., Shimizu, M., 1988. Mercurian gold from the Tsugu gold-antimony vein deposit in Japan. *Can. Mineral.* 26, 423–428.
- Smith, M.P., Gleeson, S.A., Yardley, B.W.D., 2013. Hydrothermal fluid evolution and metal transport in the Kiruna District, Sweden: Contrasting metal behavior in aqueous and aqueous–carbonic brines. *Geochim. Cosmochim. Acta* 102, 89–112.
- Spiridonov, E.M., Pletnev, P.A., 2002. The Zolotaya Gora Copper Gold Deposit (in the Context of Gold–Rodingite Assemblage). Nauchnyi Mir, Moscow (in Russian).
- Sundman, B., Fries, S., Oates, W., 1998. A thermodynamic assessment of the Au–Cu system. *Calphad* 22, 335–354.
- Tanger, J.C., Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for standard partial molal properties of ions and electrolytes. *Am. J. Sci.* 288, 19–98.
- Townley, B.K., Herail, G., Maksaev, V., Palacios, C., Parseval, P., Sepulveda, F., Orellana, R., Rivas, P., Ulloa, C., 2003. Gold grain morphology and composition as an exploration tool: application to gold exploration in covered areas. *Geochem. Explor. Environ. Anal.* 3, 29–38.
- Wanhainen, C., Broman, C., Martinsson, O., 2003. The Aitik Cu–Au–Ag deposit in Northern Sweden: a product of high salinity fluids. *Mineral. Deposita* 38, 715–726.
- Wanhainen, C., Broman, C., Martinsson, O., Magnor, B., 2012. Modification of a palaeoproterozoic porphyry-like system: Integration of structural, geochemical, petrographic, and fluid inclusion data from the Aitik Cu–Au–Ag deposit, Northern Sweden. *Ore Geol. Rev.* 48, 306–331.
- White, J.L., Orr, R.L., Hultgren, R., 1957. Thermodynamic properties of silver–gold alloys. *Acta Metall.* 5, 747–760.
- Xie, Y.Q., Li, X.B., Liu, X.B., Nie, Y.Z., Peng, H.J., 2014a. Alloy gene Gibbs energy partition function and equilibrium holographic network phase diagrams of AuCu<sub>3</sub>-type sublattice system. *Trans. Nonferrous Met. Soc. China* 24, 3585–3610.
- Xie, Y.Q., Peng, H.J., Liu, X.B., Liu, X.B., Nie, Y.Z., 2014b. New atom movement mechanism for tracking path on disordering AuCu (A<sub>8</sub><sup>Au</sup>A<sub>4</sub><sup>Cu</sup>) compound. *Trans. Nonferrous Met. Soc. China* 24, 3221–3256.
- Xie, Y.Q., Nie, Y.Z., Li, X.B., Peng, H.J., Liu, X.B., 2015. Alloy gene Gibbs energy partition function and equilibrium holographic network phase diagrams of Au<sub>3</sub>Cu-type sublattice system. *Trans. Nonferrous Met. Soc. China* 25, 211–240.
- Yokokawa, H., 1988. Tables of thermodynamic properties of inorganic compounds. *J. Nat. Chem. Lab. Indus., Tsukuba Ibaraki, Jap.* 83, 27–118.
- Zaikov, V.V., Melekestseva, I.Yu., 2011. Minerals of gold and silver in the ore facies in gold–sulfide–base-metal deposits of the Baimak ore region, South Urals. *Litosfera* 6, 47–67 (in Russian).
- Zaikov, V.V., Tairov, A.D., Zaikova, E.V., Kotliarov, V.A., Yablonsky, L.T., 2012. Precious Metals in Ores and Ancient Gold Products of the Southern Urals. RIO UrB RAS, Yekaterinburg (in Russian).