ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 8, pp. 744–757. © Pleiades Publishing, Ltd., 2007.
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Geochemical Mobility of Au and Ag during Hydrothermal Transfer and Precipitation: Thermodynamic Simulation

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Received January 24, 2006

Abstract—The thermodynamic simulation of the geochemical mobility of Au and Ag during their hydrothermal transfer and precipitation was conducted with regard for the formation of continuous nonideal Au–Ag solid solutions (or Au_XAg_{1-X}) alloys) and with the analysis of the effects of principal physicochemical parameters (temperature, pH, redox potential, and the concentrations of sulfide sulfur and chloride ions) on the solubility of Au–Ag alloys of various composition. Predominant Au and Ag complexes and the types of solutions were identified, which are characterized by different extractive ability with respect to these metals. A tendency in the variations in the Au/Ag ratio in the solid phase during the evolution of the hydrothermal process was revealed with regard for various conditions under which Ag sulfides can occur. The possible effect of the Au_XAg_{1-X}/solution ratio on the composition of the Au–Ag mineralization was demonstrated, and tendencies in the variations in the composition (fineness) of the alloys during their redeposition were identified.

DOI: 10.1134/S0016702907080022

INTRODUCTION

In modeling the conditions under which Au and Ag deposits are formed, most researchers limit themselves to the consideration of these metals as pure components. We also applied this approach in our earlier research devoted to the role of carbon dioxide in the geochemical processes of gold transfer and precipitation [1, 2]. However, natural native gold always contains admixtures of other metals, first of all, silver [3–5]. Analogously, gold can occur in significant amounts as an admixture in native silver [6, 7]. According to one of the two currently most popular viewpoints, gold and silver compose a continuous series of solid solutions Au_XAg_{1-X} [8, 9]. The proponents of the other concept believe that this series is composed of intermetallic compounds with the proposed stoichiometry Au_8Ag, Au_3Ag, Au_2Ag, and $AuAg_3$ [4, 5, 10]. In any event, the conventionally adopted measure of Au concentration in an artificial alloy or a natural gold grain or nugget is gold fineness (N_{Au}), which is equal to Au/(Au + Ag) $\frac{Au}{Au + Ag}$ × 1000 (in weight promille), which can vary from 1000 to 0. Since no scale for gold fineness has been universally adopted as of yet, in characterizing the composition of native gold and silver, we adhered to the terminology applied in [3, 5]: high-fineness gold for 1000–700 gold fineness (the composition of the gold–silver alloys expressed in mole fractions is $Ag_{0.0}Au_{1.0}$–$Ag_{0.44}Au_{0.56}$), electrum for 700–250 ($Ag_{0.44}Au_{0.56}$– $Ag_{0.85}Au_{0.15}$), kustelite for 250–100 ($Ag_{0.85}Au_{0.15}$–$Ag_{0.94}Au_{0.06}$), native silver for < 100 ($Ag_{0.94}Au_{0.06}$–$Ag_{1.0}Au_{0.0}$)).

This parameter is thought to be controlled by the conditions under which the ores were formed, and an increase in gold fineness is sometimes believed to be related to an increase in the depth and/or temperature [3, 5]. The proponents of another viewpoint believe that gold fineness is controlled by such parameters as redox potential, acidity–alkalinity, and the composition of the solutions [11–15]. Some publications were devoted to geochemical control on gold fineness and its role as a potential prospecting guide [16–17]. We believe that the problem of the thermodynamic simulation of Au and Ag behavior was accurately enough formulated first in [13] and then in [18], whose authors analyzed the principal tendencies in variations in the composition of the aqueous solutions and Au–Ag alloy being in equilibrium with them related to a number of specified physicochemical situations. These researchers did not, however, allow for the possibility of the occurrence of monohydrosulfide complexes of Au and Ag. Our research was aimed at the thermodynamic simulation of coupled Au and Ag behaviors in hydrothermal chloride–sulfide solutions and at the revealing of the systematic variations in the Au/Ag ratio in Au–Ag alloys assumed to be in equilibrium with these solutions. In fact, we returned to the problem first formulated by Goldschmidt [19], later more thoroughly analyzed by Shcherbina from the geochemical viewpoint [20], and now often discussed in numerous publications devoted to a broad spectrum of problems [21, 22]. Our model is aimed at revealing and comparing the geochemical mobility of gold and silver depending on temperature and the composition of solution in equilibrium with gold–silver alloys. Finally, the problem formulated in our research can be defined within the framework of the terminology adopted by followers of Korzhinskii [23] as the identification of the physicochemical conditions under which gold and silver can pass from their inert state (with a very low solubility) to a perfectly mobile state (which ensures the possibility of the input or removal of a component with limited portions of solutions).

THERMODYNAMIC DATABASE

Based on available experimental and theoretical information, we developed an extended thermodynamic database for the major complex species of gold and silver that are thought to predominantly control the transfer of these metals with hydrothermal solutions. First of all, we relied on the theoretical reviews [24–27], which present a fairly detailed analysis of thermodynamic constants for Au and Ag complexes within broad temperature and pressure ranges. We also utilized our experience in the critical assessment of the $AgHS^0$ and $AuHS^0$ monosulfide complexes [28, 29]. For the Au–Ag–Na–Cl–S–H_2O system studied in the course of our research, we compiled two sets of thermodynamic constants. In Table 1, 1 marks the thermodynamic database that was used in this research as the basis for the calculations of the simultaneous Au and Ag solubility in sulfide–chloride solutions. The database includes data on $AuCl^0$, $AuCl_2^-$, $AuCl_3^{2-}$, $AgCl^0$, $AgCl_2^-$, $AlCl_3^{2-}$, $AgCl_4^{3-}$, $Au(HS)_2^-$, and $Ag(HS)_2^-$ compiled from [26] and data on $AgOH^0$, $Ag(OH)_2^-$, Ag^+, and Au^+ compiled from [25], which were supplemented with data on the $AuOH^0$ and $Au(OH)_2^-$ complexes from the UNITHERM database [27] and on $AgHS^0$ and $AuHS^0$ form [29]. For comparison, in calculating the constants of exchange reactions and the *T–P* stability fields of Au and Ag complexes, we also used an additional second database that included the free energy values for hydrosulfide, chloride, and hydroxide complexes of gold and silver and their ions (this database in marked with 2 in Table 1). These data were calculated from the thermodynamic characteristics from [24]. Their simultaneous application allowed us to estimate the possible extent of the discrepancies between the calculation results related to individual uncertainties in the input thermodynamic information. Table 1 also lists the Gibbs free energy values for some Au and Ag complexes calculated with the use of later experimental results from [30–33]. It should be mentioned that, according to the results of numerous experimental studies, the scatter in the thermodynamic characteristics of Au and Ag is fairly significant (particularly at temperatures higher than 300°C) and not always can be interpreted unambiguously. Moreover it is still uncertain what the stoichiometry of the neutral complex that was interpreted as $AuHS^0$ and/or $Au(H_2S)(HS)^0$ is [34–40]. We chose the stoichiometric variant $AuHS^0$ and, correspondingly, $AgHS^0$. Until recently no monohydrosulfide Au and Ag complexes were taken into account in the thermodynamic analysis of the conditions under which natural mineral deposits were formed [18, 41–44]. At the same time, their important, if not determining, role in the geochemical transfer of Au and Ag is now quite obvious, particularly for near-neutral solutions with moderate concentrations of chlorides and H_2S [45–49].

The thermodynamic characteristics of predominant solute species in the Na–Cl–S–H_2O system were borrowed from SUPCRT92 [50]. To maintain internal consistency within databases 1 and 2, data on HCl, H_2S, and OH^- were compiled from different sources and are listed in Table 1. For the $NaHS^0$ species, thermodynamic characteristics were evaluated (following [51]) by means of equalizing its dissociation constants to those of NaCl with the subsequent recalculation to the free energy values and evaluation of the parameters of the HKF equation.

The thermodynamic characteristics of minerals that can appear in the system Ag–Au–Na–Cl–S–H_2O (Ag—silver; Au—gold; α- and β-Ag_2S—acanthite and argentite; AgCl–chlorargyrite; S—sulfur; Ag_3AuS_2—uytenbogaardtite; and AgAuS—petrovskaite) were compiled from [52, 53]. The formation of Au–Ag solid solutions was taken into account in compliance with the nonideal mixing model between Au and Ag [54] and with regard for the possibility of the formation of $Ag_2S - Au_2S$ solid solutions within a broad temperature range according to the ideal mixing model for the end members of this series, with the use of data on the G_T for gold sulfide from [52].

The thermodynamic calculations were carried out for the temperature range of 100–500°C, which is the most typical for the development of hydrothermal Au and Ag deposits [7, 55]. Inasmuch as relatively low pressures were determined for these deposits, usually 100–1000 bar and only occasionally as high as 2000 bar, according to [56], and variations in this parameter insignificantly affect the solid-state transformations and properties of aqueous species; in our calculations we assumed $P = 1000$ bar. Since pyrite is a sulfide that commonly occurs in these associations and is one of the principal Au concentrators [57, 58], some principal boundary conditions assumed for the model were the temperature functions of the redox potential and sulfur concentration corresponding to the conditions of the reduced pyrite–pyrrhotite (magnetite) (*Py–Po*) or oxidized hematite–pyrite (magnetite) (*Hem–Py*) buffer. The equilibrium oxygen or hydrogen fugacity values ($\log f_{O_2}$ and $\log f_{H_2}$), as well as those of gaseous sulfur in the form of S_2 ($\log f_{S_2}$), for the specified buffers

Table 1. Gibbs free energy values G_T (kcal/mol) for aqueous Au and Ag species and aquated HCl, H_2S, and OH^- ions for temperatures of 100–500°C (P = 1000 bar) used in this research (compiled from various sources)

Species	Reference	$G_{T°C}$						DB*
		100	200	300	350	400	500	
Ag^+	[25], [27]	17.06	14.97	12.70	11.51	10.30	7.80	1
	[24]	17.01	14.71	12.09	10.69	9.24	6.21	2
$AgHS^0$	this paper	–1.70	–3.52	–5.42	–6.41	–7.42	–9.55	1
	[27]	–1.69	–3.84	–5.33	–5.67	–5.57	–3.19	–
	[30]	–0.61	–2.21	–4.39	–5.60	–6.87	–	–**
	[24]	0.66	–3.12	–7.06	–9.08	–11.13	–15.30	2
$Ag(HS)_2^-$	[26]	–2.51	–6.70	–11.40	–14.30	–17.99	–30.32	1
	[27]	–2.91	–7.83	–12.09	–13.81	–15.12	–15.40	–
	[30]	–7.0	–12.22	–17.41	–19.63	–21.62		–**
	[24]	–2.39	–7.49	–12.61	–15.11	–17.51	–21.57	2
$AgCl^0$	[26]	–19.44	–23.14	–27.06	–29.10	–31.19	–35.53	1
	[24]	–19.27	–22.46	–25.71	–27.35	–29.00	–32.34	2
$AgCl_2^-$	[26]	–53.87	–58.87	–63.88	–66.26	–68.39	–71.06	1
	[24]	–54.08	–58.81	–63.35	–65.49	–67.47	–70.55	2
$AgCl_3^{2-}$	[26]	–84.14	–88.94	–93.49	–95.44	–96.84	–97.43	1
$AgCl_4^{3-}$	[26]	–112.24	–116.21	–119.65	–120.84	–121.38	–118.61	1
$AgOH^0$	[25]	–22.99	–24.56	–26.13	–26.91	–27.70	–29.34	1
	[24]	–23.59	–26.54	–30.06	–31.99	–34.03	–38.39	2
$AgO^-/Ag(OH)_2^-$	[25]	–6.45	–7.16	–7.28	–7.03	–6.50	–3.95	1
	(+H_2O)	(–64.10)	(–67.07)	(–69.83)	(–71.03)	(–72.03)	(–72.77)	–
	[24]	–63.05	–64.12	–64.74	–64.79	–64.58	–62.72	2
Au^+	[25]	37.40	34.73	31.96	30.56	29.14	26.30	1
	[24]	38.52	36.74	34.85	33.88	32.89	30.89	2
$AuHS^0$	[28]	3.47	–0.56	–4.53	–6.49	–8.46	–12.42	1
	[27]	5.98	1.30	–3.25	–5.44	–7.55	–11.08	–
	[24]	4.63	0.76	–2.77	–4.43	–6.01	–9.00	2
	[31]	–	–1.86	–5.91	–7.62	–9.00	–	**
	[32]				–8.71	–8.69		**
$Au(HS)_2^-$	[26]	–0.11	–6.03	–12.00	–14.91	–17.70	–22.34	1
	[27]	–2.53	–7.93	–12.58	–14.47	–15.93	–16.44	–
	[24]	–0.73	–6.37	–11.74	–14.25	–16.56	–20.03	2
	[32]				–18.88	–20.33		**
$AuCl^0$	[26]	–5.29	–9.29	–13.31	–15.32	–17.35	–21.49	1
	[24]	–4.93	–8.82	–12.64	–14.53	–16.41	–20.13	2
$AuCl_2^-$	[26]	–39.00	–43.81	–48.26	–50.28	–52.09	–54.52	1
	[24]	–38.62	–43.36	–48.25	–50.65	–52.94	–56.57	2
$AuCl_3^{2-}$	[26]	–69.72	–74.80	–78.96	–80.52	–81.55	–80.70	1

Table 1. (Contd.)

Species	Reference	$G_{T°C}$						DB*
		100	200	300	350	400	500	
$AuOH^0$	[27]	–26.14	–30.45	–35.07	–37.43	–39.79	–44.34	1
	[33]	–30.56	–33.34	–35.43	–36.24	–40.31	–42.06	***
	[24]	–33.48	–35.44	–37.33	–38.25	–39.16	–40.94	2
$Au(OH)_2^-$	[27]	–72.65	–76.21	–79.53	–80.84	–81.70	–81.16	1
	[24]	–66.69	–67.23	–67.28	–67.05	–66.58	–64.37	2
HCl^0	[26]	–30.86	–32.06	–33.94	–35.20	–36.76	–41.46	1
	[24]	–29.92	–31.28	–33.71	–35.24	–36.96	–40.92	2
H_2S^0	[26]	–8.41	–12.68	–17.71	–20.48	–23.41	–29.82	1
	[24]	–8.66	–12.86	–17.55	–20.04	–22.61	–28.00	2
OH^-	[25]	–155.89	–151.84	–145.19	–140.61	–134.90	–118.32	1
	[27]	–155.79	–152.35	–146.48	–141.80	–135.20	–112.90	2

Notes: * DB—our databases used in the calculates,
** P = 500 bar;
*** P = 1000 bar, calculated with the use of constants from [33] and $G_T(Au^+)$ and $G_T(OH^-)$ from [25].

were borrowed from [59, 60]. Most of our calculations of simultaneous Au and Ag dissolution were carried out by the HCh computer program for the minimization of the free energy [27]. The equilibrium compositions of Au-Ag solid solutions were calculated either by using the constants of exchange reactions between Au and Ag with corrections introduced for the activity coefficients of the metals or by utilizing the additional ELECTRUM module [54], which was developed as a supplement for the HCh program.

EFFECT OF PHYSICOCHEMICAL PARAMETERS ON THE SOLUBILITY OF GOLD–SILVER ALLOYS

The main task of this research was the simulation of the possible effect of physicochemical parameters on the solubility of Au–Ag alloys of various composition in hydrothermal processes. One of the assumed model solutions was 1.0 m aqueous NaCl solution, whose composition corresponded to 6 wt % NaCl (or 60 g of NaCl per 1 kg of H_2O), which characterizes the limiting concentrations of salts in low Cl solutions detected at some gold deposits. Figure 1a shows the equilibrium concentrations of metals that passed into the 1.0 m aqueous NaCl solution interacting with various amounts of alloys of the gold–silver series, including the end members, at 300°C, in the presence of the *Py–Po* buffer. Specifying varying amounts of the alloys (with respect to 1 kg of H_2O) of various initial composition, we determined the extractive ability of the solution with respect to Au and Ag needed to form the equilibrium associations. This eventually allowed us to evaluate the mobility of Au and Ag and to calculate the composition of Au–Ag mineralization and the fineness of native gold produced under various physicochemical parameters. When the values of Au_XAg_{1-X}/1 kg of H_2O (which is denoted q) are low ($<10^{-7}$) (Fig. 1a), Au and Ag pass into solution in proportions corresponding to the initial concentrations of these metals in the alloy. At average q values from 10^{-7}–$10^{-5.5}$, the solution is in equilibrium with "pure" gold or alloys of higher fineness than the original values (Fig. 1b). At $q > 10^{-5.5}$, "pure" silver dissolves with the formation of argentite. The appearance of Ag_2S in association with the alloy is controlled by the Au/Ag ratio in the original Au_XAg_{1-X} composition. If Au/Ag > 0.7 (which corresponds to metal ratios in the alloy in equilibrium with Ag sulfide at a given temperature in the presence of the pyrrhotite-bearing buffer), then the alloys produced at 300°C have a higher fineness than the original one, as in the case with the composition $Au_{0.35}Ag_{0.65}$ (fineness 500, Au/Ag = 1) and without Ag sulfide. If the ratio Au/Ag < 0.7, then, for example, alloy of original composition $Au_{0.06}Ag_{0.94}$ (fineness 100, Au/Ag = 0.11) dissolves with the formation of argentite and alloy $Au_{0.29}Ag_{0.71}$ (fineness 430, Au/Ag = 0.7). The ratio of the molal concentrations of the metals $(m_{Au}/m_{Ag})_{aq}$ [and the weight proportions $(Au/Ag)_{aq}$] in the solutions are at a minimum for the association of the alloy with silver sulfide (Fig. 1c) and increase with increasing fineness of the equilibrium composition of the alloy. Note that the fineness of the alloy in equilibrium with Ag_2S is controlled by temperature, concentrations of sulfide sulfur, and redox conditions, i.e., the *Py–Po* buffer in the situation considered here.

Table 2 presents the results of our calculations of gold fineness and the Au/Ag ratios (weight) that characterized the composition of the gold–silver mineralization ($Au_XAg_{1-X} + Ag_2S$ or Au_XAg_{1-X}) and the theoretically possible temperature at which native gold is formed at the conditions of the pyrite-bearing buffer. The association of Ag sulfide at high temperatures (500–400°C) is in equilibrium with high-fineness gold. As the temperature decreases to 200°C, its fineness decreases with the formation of, first, electrum and then kustelite. At lower temperatures, the origin of native silver can be expected. It should be mentioned that the Au/Ag ratios (or the Ag concentration) in native Au at the same temperatures are higher in association with Ag_2S, and, hence, the gold fineness is lower for the reduced pyrrhotite-bearing buffer than for the more oxidizing but "less sulfide" hematite-bearing buffer. It should also be taken into account that the high fineness of native gold and high Au/Ag ratios in pyrite-bearing ores in the absence of Ag sulfide in the Au–Ag mineralization are not always indicative of high temperatures, although low Au/Ag ratios in the presence of kustelite and native Ag suggest the participation of low-temperature solutions.

The effect of pH of the solutions (1.0 m NaCl + *n* m HCl or NaOH, where *n* ranges from 10^{-3}–10^{-1}) on the solubility of Au–Ag alloys and changes in their fineness at 300°C is shown in Fig. 2 ($q = 10^{-5}$). As can be seen in figure 2a, the more active transfer of Ag (as compared to that of Au) in solution during interaction with acidic chloride solutions (pH < 4) theoretically can take place with an increase in the fineness of the alloy. The fineness of electrum $Au_{0.5}Ag_{0.5}$ varies from 650 to 1000 with increasing acidity of the chloride solutions, and an increase in the alkalinity results in the shift of the equilibrium composition of the alloy toward the original composition (Fig. 2b). Kustelite is unstable, and higher fineness alloys (fineness 430–1000) are formed at pH < 4. At pH > 4, argentite and alloy are produced, with the fineness of the latter (430) corresponding to the equilibrium composition under conditions of the buffer at a given temperature. During the dissolution of "pure" silver, silver sulfide is produced over the whole pH range. Additional calculations indicate that pH at which argentite appears depends on the Ag content in the alloy and on the value of *q* (proportions of Au_XAg_{1-X}/1 kg of H_2O), i.e., when the content of Ag in the system is sufficient to form Ag_2S. As can be seen from Figs. 2a and 1a, the Au concentrations in the solution in the presence of dissolving Au–Ag alloys are characterized by intermediate values between the solubility of "pure" gold

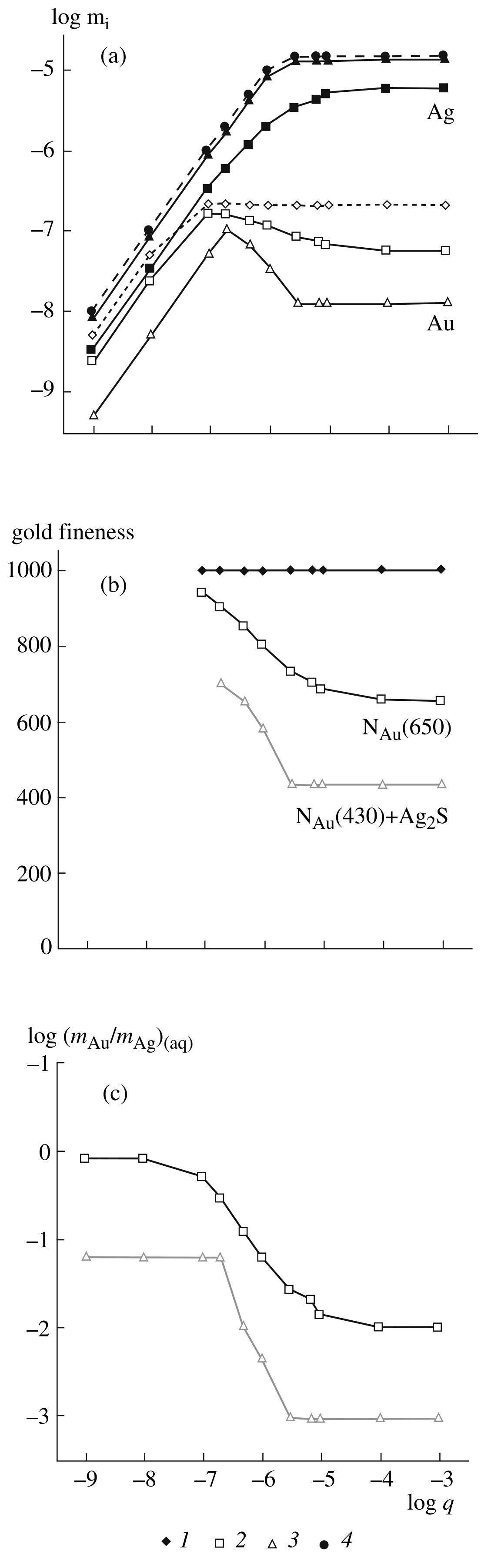


Fig. 1. (a) Total Au and Ag molal concentrations that passed into 1.0 m NaCl solution during its interaction with alloys of the Au–Ag series taken in various quantitative proportions with the solution, (b) the composition of the Au–Ag mineralization and the fineness of newly formed equilibrium alloys, and (c) the ratios of the metals in the solution. 300°C, 1000 bar, *Py–Po* buffer, *q* = alloy/kg H_2O. The initial compositions (fineness) of the alloys: (*1*) Au (1000), (*2*) $Ag_{0.65}Au_{0.35}$ (500), (*3*) $Ag_{0.94}Au_{0.06}$ (100), (*4*) Ag (0).

Table 2. Characteristics of mineral buffers, the calculated compositions of Au–Ag alloys (N_{Au}) in the presence or absence of Ag_2S (printed in bold and italics, respectively), and the Au/Ag weight ratios in the solid phases depending on temperature and the composition of the buffer association

Parameters *T*, °C	200	300	350	400	500
			Py-Po(-Mt)		
m_{H_2S}	4.4×10^{-5}	2.57×10^{-3}	9.1×10^{-3}	2.89×10^{-2}	0.23
m_{H_2}	6×10^{-6}	2.4×10^{-4}	4.4×10^{-4}	8.2×10^{-4}	3.1×10^{-3}
N_{Au}	*180 (260)**	*430 (630)*	*570 (790)*	*660 (870)*	*790 (930)*
Au/Ag (alloy + Ag_2S)	<0.2	<0.7	<1.3	<2.0	<3.9
N_{Au}	180–1000	430–1000	570–1000	660–1000	790–1000
Au/Ag (in alloys)	≥0.2	≥0.7	≥1.3	≥2.8	≥3.9
			Hem-Py(-Mt)		
m_{H_2S}	1.4×10^{-5}	5.3×10^{-4}	2.3×10^{-3}	8.7×10^{-3}	8.4×10^{-2}
m_{H_2}	6×10^{-7}	6.5×10^{-6}	1.8×10^{-5}	4.5×10^{-5}	2.5×10^{-4}
N_{Au}	*440 (680)*	*660 (890)*	*730 (920)*	*790 (950)*	*870 (970)*
Au/Ag (alloy + Ag_2S)	<0.8	<2.0	<2.7	<3.8	<6.9
N_{Au}	440–1000	660–1000	730–1000	790–1000	870–1000
Au/Ag (in alloys)	≥0.8	≥2.0	≥2.7	≥3.8	≥6.9

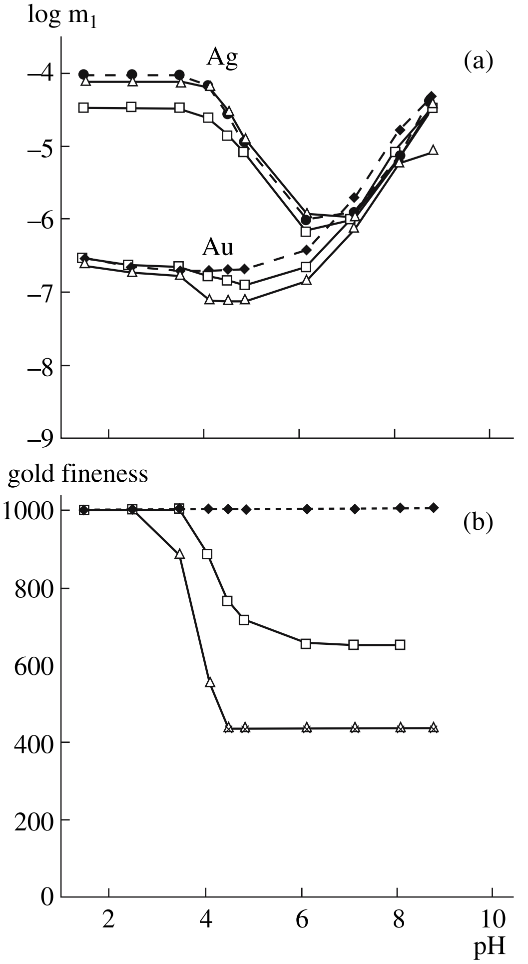
Note: * Numerals in parentheses show the fineness of the alloy according to the ideal mixing model for the metals.

and the composition of native gold in equilibrium with silver sulfide at a corresponding temperature. The Ag concentration in the solution in equilibrium with Au–Ag alloys is lower than that in equilibrium with Ag_2S. Thus, the formation of solid phases of the Au–Ag series (without Ag sulfides) requires lower concentrations of these metals in the solution.

Au AND Ag TRANSPORT SPECIES IN SULFIDE–CHLORIDE SOLUTIONS

The distribution of solute Au and Ag species depending on pH at redox conditions and sulfide sulfur concentrations corresponding to the *Py–Po* buffer (350°C, 1000 bar) are shown in Fig. 3 using the example of electrum interaction with 1.0 m NaCl solution (+ *n*m HCl or NaOH, where *n* ranges from 10^{-1}–10^{-3}). The initial alloy (of the composition $Au_{0.31}Ag_{0.69}$, $N_{Au} = 440$) taken in excess amounts is dissolved under these conditions and forms argentite and alloy 570 fine (of the composition $Au_{0.43}Ag_{0.57}$) (Table 2). Thereby the Au concentrations in the solution remain virtually unchanging because the $AuHS^0$ monosulfide complex predominates even at overall chloride concentrations equal to 1.1 m (0.1 m HCl + 1.0 m NaCl) (Fig. 3a). The amount of dissolved Ag in these solutions increases with increasing acidity (because chloride complexes of Ag dominate, first of all, $AgCl_2^-$) (Fig. 3b). In weakly alkaline solutions, the predominant dissolved Ag and Au species are their disulfide complexes. It follows from Figs. 3a and 3b also that monosulfide Au and Ag complexes should dominate in acidic and near-neutral solutions in the absence of chlorides, while weakly alkaline solutions and sulfide–chloride system should be dominated by dihydrosulfide species.

Figure 4 illustrates pH-*T* fields in which dissolved species of (a) gold and (b) silver dominate in solutions with various chloride concentrations (from 0.1 to 5 m NaCl) under redox conditions and sulfide sulfur concentrations corresponding to the pyrite–pyrrhotite (magnetite) buffer. To calculate the position of the boundaries of the principal pH-*T* fields, we used the main constants of the solubility reactions for Au and Ag, which were obtained on the basis of thermodynamic data from the two databases in Table 1. The $AuCl_2^-$ and $AgCl_2^-$ complexes were assumed as predominant among the chloride species. We were the first to take into account the $AuHS^0$ hydrosulfide complex, which occurs within a significant region of weakly acidic and near-neutral pH values in this temperature range. The fields of these complexes diminish with increasing concentrations of chlorides. The $AuCl_2^-$ complex is thereby predominant only within the region of strongly acidic solutions, and the dihydrosulfide Au species dominates only in weakly alkaline and alkaline solutions. The complex $AuCl_2^-$ also becomes predom-



Initial alloys: composition (gold fineness) ◆—Au(1000), □—$Au_{0.5}Ag_{0.5}$(650), △—$Au_{0.1}Ag_{0.9}$(170), ●—Ag(0); ×—Ag_2S.

Fig. 2. (a) Total Au and Ag concentrations and (b) equilibrium compositions of the Au–Ag alloys (N_{Au}) formed during the interaction of the original alloys of 1000, 650, 170, and 0 fineness gold with 1.0 m NaCl solutions depending on their pH. 300°C, 1000 bar, *Py–Po* buffer, alloy/kg $H_2O = 10^{-5}$.

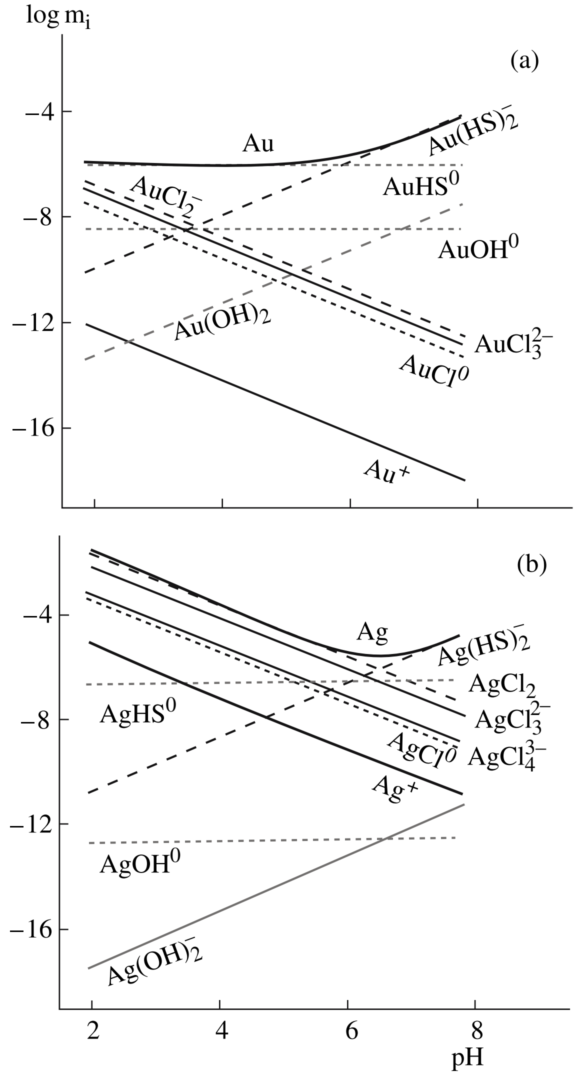


Fig. 3. Dependence of the concentrations of (a) Au and (b) Ag aqueous species on pH and the total concentrations of the metals in 1.0 m NaCl solution having various pH and interacting with electrum. 350°C, 1000 bar, *Py–Po* buffer, alloy/kg $H_2O = 10^{-2}$. Initial fineness of Au-Ag alloy is 440 ($Au_{0.30}Ag_{0.70}$), the equilibrium composition of the association: alloy 570 gold fineness 570 ($Au_{0.42}Ag_{0.58}$) and argentite.

inant in high-temperature acidic solutions already at chloride concentrations of >0.1 mol/kg H_2O. As this concentration increases, the field in which this complex is predominant expands toward near-neutral and even weakly alkaline solutions, particularly if the temperature decreases. In contrast to the complex $AuHS^0$, the monohydrosulfide Ag species $AgHS^0$ is present within relatively narrow pH and temperature ranges, particularly in concentrated chloride solutions. The complex $Au(HS)_2^-$ dominates in near-neutral and alkaline solutions, depending on the concentrations of chloride ions. To assay the possible inaccuracies of the thermodynamic calculations conducted on the basis of our data (solid lines in Fig. 4), analogous calculations were carried out with the use of constants from [24] (dashed lines). The comparison of the corresponding lines separating the fields in which the main Au compositions dominate indicates that the discrepancies between these boundaries do not exceed 0.5–0.7 pH units for $AuCl_2^-$ and 0.2–0.5 units for $Au(HS)_2^-$, whereas these discrepancies for Ag do not exceed 0.3 logarithmic units even for the $AuCl_2^-/Ag(HS)_2^-$ boundary line. Note that the pH-*T* fields in which Au and Ag complexes dominate in solutions with various chloride concentrations (from 0.1 to 5 m NaCl) coincide within this accuracy for the *Hem–Py* and *Py–Po* buffers.

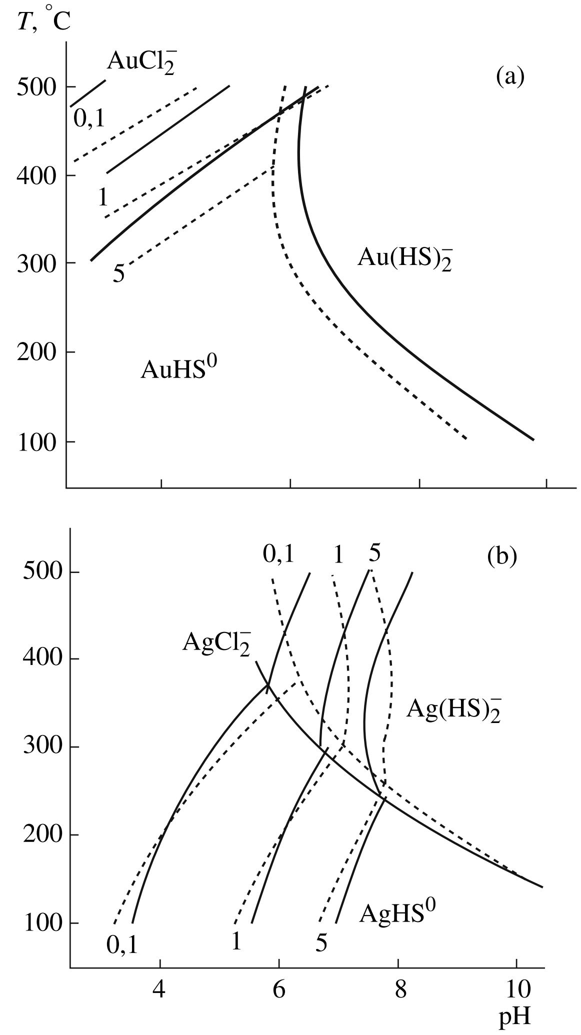


Fig. 4. T-pH stability fields of (a) Au and (b) Ag complexes in solutions with NaCl concentrations from 0.1 to 5 m. 1000 bar, *Py–Po* or *Hem–Py* buffer. Solid and dashed lines correspond to the first and second thermodynamic databases. Numerals near lines are NaCl concentrations (mol).

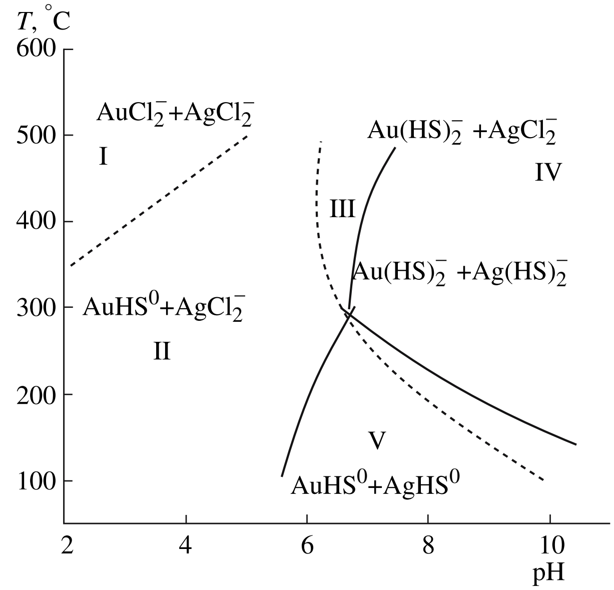


Fig. 5. T–pH stability fields of Au and Ag complexes and the most typical possible situations with the proportions of their predominant species in chloride–sulfide solutions at the formation of pyrite-bearing associations: (I) AuCl$_2^-$, AgCl$_2^-$; (II) AgCl$_2^-$, AuHS^0; (III) AgCl$_2^-$, Au(HS)$_2^-$; (IV) Ag(HS)$_2^-$, Au(HS)$_2^-$; (V) AgHS^0, AuHS^0. Solid lines divide fields in which various Ag complexes dominate at moderate (6 wt % NaCl) concentrations of chlorides, dashed lines are analogous boundaries for Au complexes.

In order to reveal the main combinations of the main complexes during the simultaneous transport of the metals with hydrothermal sulfide–chloride solutions, their stability fields were combined as is shown in Fig. 5 in the variant for solutions with 1.0 m concentration of NaCl. It was determined that, depending on temperature, pH, and chloride concentration in the solutions, the following five principal fields can be recognized, along with the corresponding types of ore-forming solutions with certain compositions of predominant Au and Ag complexes, which are characterized by potentially different geochemical behavior of Au and Ag. Field I presents a relatively small area of high-temperature acidic solutions (solutions of type I) in which both metals are present in the form of dichloride complexes AuCl$_2^-$ and AgCl$_2^-$. At low and moderate pH (5–7) and fairly high temperatures, which decrease with increasing chloride concentration (solutions of type II), gold is contained in the solutions predominantly in the form of the monohydrosulfide complex AuHS^0. At the same time, the relatively higher stability of the chloride complex AgCl$_2^-$ makes it predominant over broad temperature and pH ranges. Another variant, in which the predominant Au and Ag species have a different ligand composition, is possible within a relatively narrow range of high-temperature near-neutral and weakly alkaline (pH 6–8) chloride–sulfide solutions (solutions of type III). In these solutions, Ag still remains in the form of chlorides at moderate chloride concentrations, while Au already passes into the Au(HS)$_2^-$ disulfide complex.

Field IV corresponds to conditions under which both metals are contained in the solutions in the form of dihydrosulfide complexes. In this form, both gold and silver are transported by near-neutral or alkaline solutions at pH 6–10 depending on the concentrations of chlorides, which can range from 0 to 5 m NaCl and more (solutions of type IV). The predominance of monohydrosulfide Au and Ag complexes throughout the whole temperature range in question at pH < 6 is possible either in the absence of chlorides or in the presence of moderate (at $m_{NaCl} < 1.0$ mol/kg H_2O) con-

Table 3. Equations and constants of the main exchange reactions for temperatures of 100–500°C and a pressure of 1000 bar

no.	Equation	*T* °C						Reference	Solution type
		100	200	300	350	400	500		
1	$Au_{alloy} + AgCl_2^- \rightleftarrows Ag_{alloy} + AuCl_2^-$	–8.76	–7.05	–6.08	–5.73	–5.44	–4.83	1	I
		–9.11	–7.23	–5.88	–5.34	–4.86	–4.11	2	
2*	$Au_{alloy} + H_2S_{aq} + AgCl_2^-$	–1.35	–3.01	–4.95	–5.96	–7.01	–9.26	1	II
	$\rightleftarrows Ag_{alloy} + 2Cl^- + H^+ + AuHS^0$	–2.15	–3.60	–5.41	–6.42	–7.51	–10.08	2	
3	$Au_{alloy} + AgCl_2^- + 2H_2S_{aq}$	–4.18	–6.35	–8.85	–10.19	–11.62	–14.88	1	III
	$\rightleftarrows Ag_{alloy} + Au(HS)_2^- + 2Cl^- + 2H^+$	–3.94	–6.16	–8.75	–10.16	–11.68	–15.39	2	
4	$Au_{alloy} + Ag(HS)_2^- \rightleftarrows Ag_{alloy} + Au(HS)_2^-$	–1.46	–0.41	0.10	0.08	–0.24	–2.41	1	IV
		–1.03	–0.61	–0.45	–0.44	–0.45	–0.59	2	
5*	$Au_{alloy} + AgHS^0 \rightleftarrows Ag_{alloy} + AuHS^0$	–3.08	–1.46	–0.46	–0.1	0.19	0.66	1	V
		–3.74	–2.07	–1.14	–0.82	–0.60	–0.31	2	
		–2.96	–1.35	–0.64	–0.35	–0.27	–0.02	3	
6	$Ag_{alloy} + 0.5H_2S_{aq} \rightleftarrows 0.5Ag_2S + 0.5H_{2aq}$	–0.42	–0.34	–0.23	–0.23	–0.18	0.01	1	I–V
		–0.50	–0.38	–0.19	–0.09	0.01	0.26	2	

Note: * The reactions are not included into consideration in [13, 18]; (1) this paper; (2) [24]; (3) [27].

centrations of NaCl, but only at temperatures no higher than 300°C (solutions of type V).

Au AND Ag EXCHANGE REACTIONS AND ASSESSMENT OF NATIVE GOLD FINENESS

The behavior of Au and Ag in hydrothermal processes at various physicochemical parameters is controlled, first of all, by the stability of their solute species and solid phases. Table 3 lists the equations and constant values of principal exchange reactions (1)–(5), which characterize the solubility of Au–Ag alloys (without the formation of Ag_2S) in sulfide–chloride solutions in compliance with the composition of the predominant Au and Ag complexes at temperatures of 100–500°C ($P = 1000$ bar). It is important to emphasize that the expressions for the constants of these reactions are special cases of the equation $(a_{Au}/a_{Ag})_{alloy} = K_i (a_{Au}/a_{Ag})_{aq} \cdot a^n_{H_2S}{}^*/(a^p_{Cl}a^q_{H^+})$, which makes it possible to relate the composition of Au–Ag alloy (through the equilibrium constant of reaction i K_i) with the mass proportions of such principal components of the solution as the H^+ ion, sulfide sulfur, and chlorides, the main complex-forming components. The concentration of H_2S_{aq} corresponds to the values assumed in our model (Table 2), and n, p, and q are the stoichiometric coefficients of reaction i. Reaction (6) describes the formation of Ag sulfide when Au–Ag alloys interact with sulfide solutions. No appearance of Ag_2S–Au_2S solid solutions or phases of the composition Ag_3AuS_2 and AgAuS in the examined ranges of the physicochemical parameters was detected. Reactions (1), (4), and (5) control the equilibria of the alloys with solutions of types I, IV, and V, when Au and Ag are transferred in the form of dichloride and di- and monohydrosulfide complexes. Reactions (2) and (3) characterize solutions of types II and III, which are able to transport the metals in the form of dichloride Ag complexes and di- or monohydrosulfide complexes of Au.

Using the constants of exchange reactions (1)–(5) and correcting them for the activity coefficients of metals in the alloy [61], we calculated the fineness of native gold produced under conditions buffered by pyrite-bearing mineral assemblages according to the predominant Au and Ag transport species in solutions. Our estimates for the composition of native gold in the presence or absence of silver sulfides are presented in a generalized form in Fig. 6. If Au and Ag are transported as mono- and dihydrosulfide complexes, the fineness of the native gold precipitating from solutions of types IV and V is controlled by the $(Au/Ag)_{aq}$ ratio and the constants of reactions (4) and (5), which, in turn, are controlled mainly by temperature. The fineness of gold can be higher at 200 than at 300°C at $(Au/Ag)_{aq}$ = const. It is much more difficult to assay the Ag concentration in the native Au precipitated by solutions of type II or III, because this parameter is dependent not only on Au and Ag concentrations in the solution and the constants of exchange reactions (2) and (3) but also by the relations between a_{H_2S}, a_{Cl^-}, and pH. For brevity, these components are denoted $Q = M + L$ in Fig. 6,

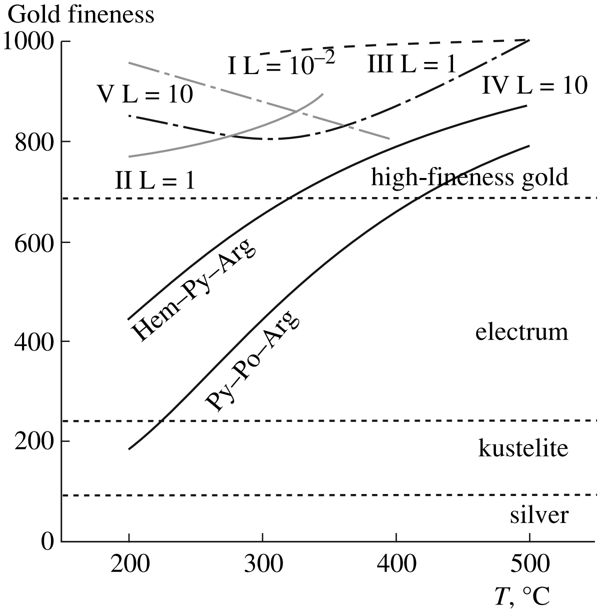
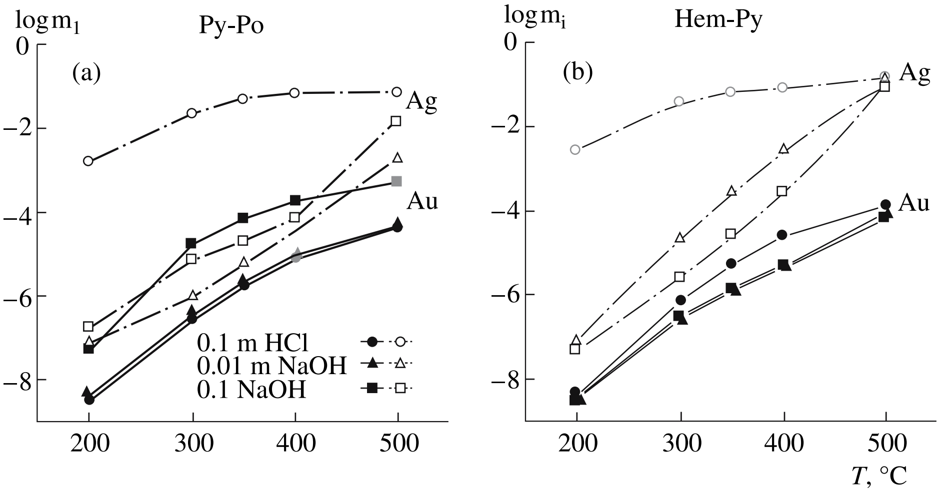


Fig. 6. Temperature dependences of the fineness of native gold in equilibrium with solutions of various types (I–V). Solid lines show alloy in association with silver sulfide, dashed and dash-dot lines show only alloy.
Py–Po or *Hem–Py* buffers $L = m_{Au}/m_{Ag}$ (solutions of types I, IV, and V), $Q = (m_{Au}/m_{Ag})a^p_{Cl}a^q_{H^+}/m^n_{H_2S}$ (solutions of types II and III).

where $M = a^p_{Cl}a^q_{H^+}$, which depends on the type and form of expression for the equilibrium reaction of the alloy and solution of given composition, and $L = a_{Au}/a_{Ag}$ is the ratio of the Au and Ag activities in the solution. The fineness should decrease with increasing concentrations of chlorides and alkalinity, as well as with decreasing temperature. It is worth mentioning that discrepancies between the gold fineness values calculated with the application of the first and second thermodynamic databases generally do not exceed 100 units.

POSSIBLE Au/Ag RATIOS IN THE SOLUTIONS AS A FUNCTION OF THE EVOLUTION OF THE PHYSICOCHEMICAL PARAMETERS AND COMPOSITION OF THE SYSTEM

The diagrams presented below may be interesting from two standpoints. They characterize the mobility of Au and Ag and the evolution of the possible concentrations of these metals in ore-forming solutions. Figures 7a and 7b quantitatively characterize the maximum mobility of Au and Ag at reduced (pyrrhotite-bearing) or oxidized (hematite-bearing) mineral buffers depending on the temperature and pH of the solutions. It is thereby assumed that 1.0 m NaCl aqueous solution participates in the acidic variant (additionally introduced HCl in the proportion 0.1 mol/kg H_2O), alkaline variant (NaOH introduced in the proportion 0.1 mol/kg H_2O), and in the variant of weakly alkaline solutions (0.001 mol NaOH/kg of H_2O). It is reasonable to expect that Ag is highly mobile in acidic solutions at the inert behavior of Au throughout the whole temperature range, regardless of the composition of the mineral buffers. At the same time, starting at a temperature of 300°C, the concentration lines for these metals are spaced fairly closely, particularly for strongly alkaline solutions, and the mobil-



0.1 m HCl	pH 1.2	1.5	1.8	2.5	3.1	pH	1.2	1.5	1.7	1.9	2.7
0.01 m NaOH	7.0	6.0	5.8	5.7	5.8		6.1	4.9	4.5	4.3	4.2
0.1 NaOH	9.5	9.0	9.1	9.2	9.7		7.0	5.9	5.5	5.3	4.6

Fig. 7. Total Au and Ag concentrations passing into 1.0 m NaCl solutions of various pH during their interaction with the end members of the Au–Ag series in the presence of (a) *Py–Po* and (b) *Hem–Py* buffers at temperatures of 200–500°C and *P* = 1000 bar.

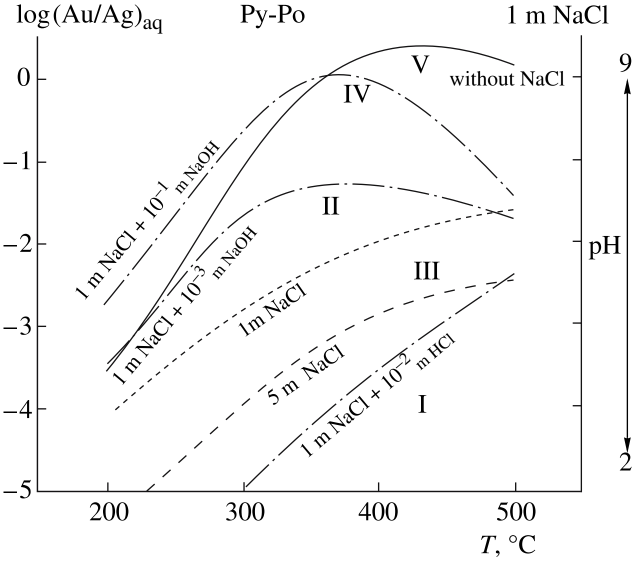


Fig. 8. Possible conjugate Au/Ag ratios in solutions with various pH at chloride concentrations from 0 to 5 m NaCl in the presence of the *Py–Po* buffer at temperatures of 100–500°C and a pressure of 1000 bar. Roman numerals correspond to the types of the solutions.

ity of Au at medium temperatures and in the presence of pyrrhotite can be even higher than the mobility of Ag. At the action of the hematite-bearing buffer, Ag definitely predominates in the strongly alkaline solutions even at low temperatures.

Figure 8 makes it possible to additionally systematize the situations with the aid of the above-distinguished five variants of the chemical composition of potentially ore-forming solutions acting in equilibrium with the pyrite-bearing buffers. Below we will use the $(Au/Ag)_{aq}$ ratio in place of (m_{Au}/m_{Ag}) because the former is more convenient when it is necessary to proceed to weight ratios of metals in alloys or solid phases. The $(Au/Ag)_{aq}$ ratios calculated above characterize solutions of various composition in equilibrium with Ag sulfide and Au–Ag alloys, whose fineness corresponds to the specified temperature and buffer. Under the conditions of the reduced pyrrhotite-bearing buffer, the lowest $(Au/Ag)_{aq}$ ratios (10^{-5} to -10^{-2}) are characteristic of strongly acidic and acidic high-chloride (6–30 wt % equiv. NaCl) high-temperature solutions, in which gold and silver are transported in the form of chloride complexes (type I solutions), as well as near-neutral high-chloride high-temperature solutions with disulfide Au complexes $Au(HS)_2^-$ and the $AgCl_2^-$ chloride Ag complex (type III solutions). The solutions with the highest $(Au/Ag)_{aq}$ ratios (from 10^{-2} to 1) are typical of alkaline solutions with any concentrations of chlorides and with disulfide transport species of the metals (solutions of type IV), as well as of chloride-free acidic or low-chloride (<6 wt % NaCl) near-neutral medium- and low-temperature solutions, which are more typical of natural processes and transport the metals as monosulfide complexes (solutions of type V). Intermediate $(Au/Ag)_{aq}$ ratios (from 10^{-3} to 10^{-2}) are characteristic of weakly acidic–near-neutral medium- and low-temperature solutions containing chloride concentrations corresponding to more than 6 wt % NaCl and the predominant $AuHS^0$ and $AgCl_2^-$ complexes (solutions of type II).

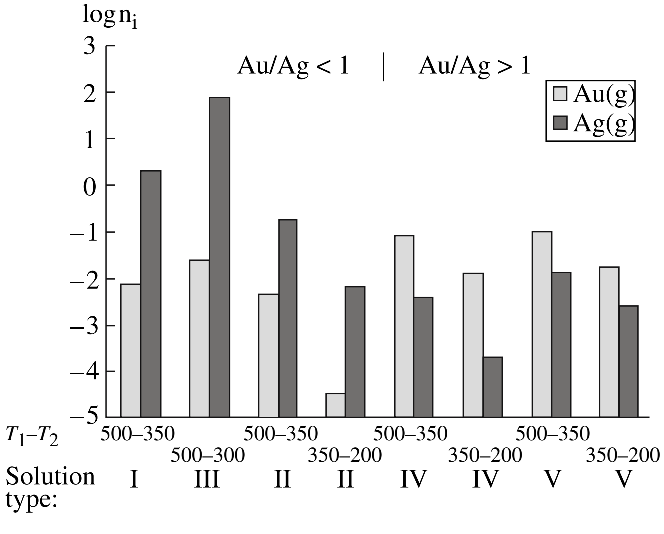


Fig. 9. Predicted amounts (in g) of Au and Ag precipitated from 1 kg of solutions of various types during their evolution as the temperature decreased within the specified ranges.

Under the conditions of the more oxidized hematite-bearing buffer, only chloride-free (which is practically improbable in natural processes) near-neutral (pH ~ 6) medium- and low-temperature solutions transporting the metals in the form of monosulfide complexes (type V) can have relatively high $(Au/Ag)_{aq}$ ratios of $>10^{-1}$. The acidic and near-neutral solutions of types I and III typically have low $(Au/Ag)_{aq}$ ratios of 10^{-3} to 10^{-5}. The solutions of type IV have $(Au/Ag)_{aq}$ ratios close to 10^{-2}. However, the pH of these solutions is closer to neutral or even acidic values, even in the presence of 0.1 m NaOH under oxidizing conditions, particularly at high temperatures, because of the appearance of oxidized S species, such as SO_2, HSO_4^-, and SO_4^{2-}. Thus, Ag turns out to be usually more mobile than inert Au in real natural solutions.

The diagram in Fig. 9 shows the possible Au and Ag amounts, predicted based on the results of our thermodynamic simulations, that can be precipitated from 1 kg of solutions of various types during their physicochemical evolution at decreasing temperature, f_{H_2}, and f_{H_2S}. The solutions of types I, II, and III theoretically can form mineralization with low Au/Ag ratios, which testify to the presence of Ag sulfide. The solutions of types IV and V are the most favorable for the precipitation of Au–Ag ores with both high Au/Ag ratios (>1) and high-fineness gold and electrum (within the range of 500 to 1000 promille gold).

CONCLUSIONS

Our thermodynamic simulations of the interrelated behavior of gold and silver in hydrothermal processes allowed us to construct a physicochemical model for the formation of native gold of various fineness. This model is applicable to the development of gold-silver-bearing mineral assemblages with pyrite, pyrrhotite, and other sulfides. We identified five principal geochemical types of solutions, which are characterized by certain extracting ability with respect to Au and Ag and their predominant aqueous species: chloride (type I), monohydrosulfide (IV), and dihydrosulfide (V), as well as chloride for Ag and hydrosulfide for Au (types II and III, respectively), depending on the physicochemical parameters. In some situations, the fineness of gold can be indicative of the Au/Ag ratios of the hydrothermal solutions and pyrite-bearing ores and of the pH and chloride concentrations in the ore-forming system. In other instances, the fineness of gold in association with argentite (acanthite) can be utilized as a geothermometer, if reliable estimates for the redox conditions and sulfide sulfur concentration are available. For example, relatively low Au/Ag ratios in solutions and sulfide ores (10^{-4} < Au/Ag < 0.1) and the formation of native gold and silver with silver sulfides can be predicted for ore-forming environments of type I. High Au/Ag > 1 and high-fineness gold and electrum in the absence of Ag_2S can supposedly be formed in environments of types IV and V. The solutions of types II and III can precipitate native gold in association with silver sulfide or without it, which is predetermined by the Au/Ag ratios within an intermediate range of 0.1 < Au/Ag < 1, the concentrations of chlorides, and pH. When ore material is redeposited as a result of native gold interaction with acidic chloride or near-neutral solutions due to the more active passage of Ag (compared to Au) into solution, the fineness of the gold can increase, which seems to take place in natural processes. The fineness of naturally occurring gold and high Au/Ag ratios in pyrite-bearing ores in the absence of silver sulfide does not always suggest that the ore-forming solutions have high temperatures.

The further studying of the stability of the phases and their equilibrium compositions in the system simultaneously containing Au and Ag requires

(1) additional information confirming that the natural mineral assemblages ubiquitously contain Au-bearing acanthite (argentite);

(2) reliable thermodynamic data on Au_2S;

(3) known values for the excess energy of mixing for solid solutions of the Ag_2S–Au_2S series.

ACKNOWLEDGMENTS

The authors thank N.N. Akinfiev, V.I. Belevantsev, and G.P. Shironosova for discussion of the manuscript. This study was supported by the Russian Foundation for Basic Research, project nos. 03-05-65056 and 06-05-96954.

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