GEOCHEMISTRY

Physicochemical Features of the Behavior of Gold and Silver in Processes of Hydrothermal Ore Formation

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As early as the late 1950s, Shcherbina [1] convincingly demonstrated the need to elucidate the specific features and causes of geochemical differentiation of Au and Ag during the formation of gold–silver deposits. A large body of data on their mineral composition and formation constraints has been accumulated and systematized to date, making it possible to carry out geological–genetic classification [2, 3]. Reviews of gold–silver deposits, in general, and papers devoted to specific deposits, in particular, have pointed out the necessity to scrutinize physicochemical features of ore-forming systems (their gold potential, mineralogical–geochemical indicators, including mineral composition of productive associations, Au/Ag ratio, gold fineness, and so on). Logic-mathematical processing of integral data on gold–silver deposits [4] also resulted in the identification of similar criteria for their typification. These facts indicate the existence of a rather limited number of typical ore–magmatic systems in nature characterized by specific thermobaric conditions, fluid phase compositions, and modes of their evolution.

The aim of the present work is to compare the main physicochemical constraints governed by basic properties of Au and Ag with general geological–geochemical trends in the formation of the major types of gold–silver deposits. Works devoted to applied geochemistry [5] and theoretical geochemistry [6] are most significant in this respect. The major features of the approach accepted in our method are schematically described in [7] and scrutinized in [8]. Data proposed in our works significantly refine the thermodynamic approach and results reported in [6]. In particular, our thermodynamic database for gold and silver complexes in solutions and alloys of the nonideal Au–Ag series has been refined and supplemented with new literature [9–11] and our data [8, 12]. Thus, we were able to obtain a more reliable thermodynamic modeling of the behavior of Au

and Ag in the six-component (Au–Ag–H_2O–H_2–NaCl–H_2S) hydrothermal system with the following independent variables: T, P, pH, f_{H_2}, c_{NaCl}, and f_{H_2S}.

Within the framework of the considered problem, all parameters listed above are crucial for the concentration (and ratio) of chloride and hydrosulfide complexes and the fineness of native gold. Formulation of the problem was based on the following assumptions: (a) the inventory of Au and Ag phases in solution is limited by the major monosulfide, dihydrosulfide, and bichloride complexes; (b) the evolution of f_{H_2} and f_{H_2S} with temperature matches conditions of the reductive Pyr–Po(–Mgt) or oxidative Hem–Pyr(–Mgt) buffers; and (c) the pressure is constant (1000 bar). Thus, we were able to reduce the thermodynamic simulation to calculation of six reaction constants for the formation of gold and silver complexes. The model also included five major reactions related to processes of exchange and formation of silver sulfide from Au–Ag alloys (see Table 1 in [8]). Based on these reactions, we revealed possible combinations of dominant soluble forms of Au and Ag depending on physicochemical parameters of the system in a temperature range of 100–500°C and NaCl concentration range of 0.6–30 wt %. We also calculated the composition of native gold in equilibrium with (or without) silver sulfide in systems with high Au contents and low Ag contents. Results of computation were checked with the HCh software package [13] providing the consideration of all chloride (and hydroxy) complexes of Au and Ag and the influence of ionic force of solutions on the activity of ions.

In order to classify the physicochemical constraints of ore formation based on the data in [8], we outlined T–pH regions dominated by the main types of solutions with specific compositions of the major Au and Ag complexes (Fig. 1). Domain I shows the high-temperature (acid) solution field where both Au and Ag are present as bichloride complexes even at a moderate chloride concentration. Domain II includes the major portion of acid–neutral solutions containing various forms of Au and Ag ($AgCl_2^-$ and $AuHS^0$) in a wide tem-

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Major types of ore-bearing solutions, characteristics of sulfide ores, and physicochemical parameters of productive stage of various genetic groups

Solution type	Characteristics of solutions			Characteristics of sulfide ores			Genetic groups /depth/ examples
	T, °C stages	C_{NaCl}, %	pH/metasomatite minerals	fineness of gold	Au/Ag*	mineral forms of Au and Ag	
I → II	480–200 1, 2	5–20	2–6/Q, Carb, Ser, Kaol, Dik, Alu, Bar, Anh	980–400	0.1–0.002	Very fine gold, electrum, **argentite**, Ag sulfosalts	**1. Gold–silver deposits in epithermal alunite–quartz formations** /<2 km/ Kairagach (Uzbekistan); Summitville (United States); Lepanto (Philippines)
I → IV	450–150 1–3	1–45	5–8/Q, Carb, Ser, Ad	700–0	1–0.0001	Electrum, küstelite, silver, **argentite**, selenides, sulfosalts, Ag intermetallides, Au and Ag tellurides	**2. Gold–silver deposits in epithermal adular–quartz formations** /<2 km/ Dukat, Kvartsevoe, Ametistovoe (Russia); Comstock, Tonopah, Patch, Gold Cap (United States), Pachuca, Guanajuato (Mexico)
I → III	700–300 1, 2	2–40	5–7/Ser, Carb, Chl	940–900 750–630	1–0.001	Very fine gold, electrum, argentite	**3. Porphyry gold–copper deposits** /2–5 km/ Kal'makyr (Uzbekistan); Santa Rita (Mexico); Bingham (United States); Kingking (Philippines)
I → II	540–240 1, 2	3–10 [20]	5–6/Chl, Q, Carb	990–600	10–1 [0.1]	Very fine gold, electrum, Au and Ag tellurides [Ag sulfosalts, **argentite**]	**4. Skarn gold deposits** (/1–5 km/ Sinyukha, Natal'evka (Russia); Ortosa (Spain); Nickel Plate (Canada); [Fortitude, Crown Jewel (United States)]
IV, II	300–200 1 350–190 2	<5–10 <20	8–6/Carb, Ser, Chl, Ad 4–6/Chl, Ser, Q, Dik	980–560 650–0	10–1 [1–0.1]	Very fine gold, electrum, calaverite, hessite, [**argentite**, Ag sulfosalts, küstelite, silver]	**5. Gold–telluride deposits** /<2 km/ Zodskoe (Armenia); Cripple Creek (United States); Emperor (Fizi); [Porgera (New Guinea); Tongjiang (Korea)
IV, II	380–220 1 400–170 2	2–5 12–30	8–6/Carb, Ser, Chl, Ab	1000–850 960–650	30–1 [3–0.1]	Very fine gold, electrum, [Ag sulfosalts, **argentite**, rare aurostibite, Au tellurides]	**6. Gold–arsenic deposits in black shales** /2–5 km/ Olimpiada (Russia); Bakyrchik (Kazakhstan); Kumtor (Kirgizia); Bendigo (Australia); [Nezhdanin (Russia)];
IV, II	400–200 1 250–180 2	1–5 5–30	8–6/Q, Carb, Ser, Ab 4–6/Q, Ser, Prf, Chl	990–900 900–530	30 – 1	Very fine gold, electrum, rare Ag sulfosalts	**7. Gold–antimony deposits** /<2 km/ Sarylakh, Uderei (Russia); Hillgrove (Australia); Karma (Bolivia); West Gore (Canada)
IV → V	380–200 1	<3	8–5/Ser, Carb, Chl	970–780	20–1	Rare Au tellurides	**8. Gold deposits in Precambrian greenstone belts** /2–12 km/ Porcupine, Bralorne (Canada); Mother Lode (United States); Ashanti (Ghana)
V → II	270–150 1	<5	7–4/Q, Kaol, decarbonatization	1000–750	300–3	Very fine gold, rare Au tellurides	**9. Gold deposits in terrigenous–carbonate formations** /2–3 km/ Carlin, Getchell, Betze-Post, Meikle (United States); Vorontsov (Russia)

Notes: Mineral abbreviations: (Q) quartz, (Kaol) kaolin, (Carb) carbonate, (Ser) sericite, (Ab) albite, (Ad) adular, (Chl) chlorite, (Prp) pyrophyllite, (Alu) alunite, (Dik) dickite, (Bar) barite, (Anh) anhydrite. Data on deposits with the intensely developed productive stage 2 are given in brackets.
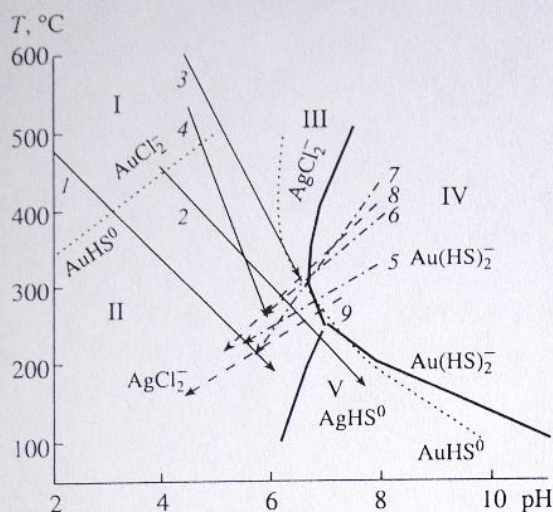
Fig. 1. Possible types of physicochemical environments and their evolution trends governing the composition of dominant Au and Ag complexes in solutions located in equilibrium with the pyrite–pyrrhotite–magnetite buffer. Heavy solid lines separate fields dominated by various silver complexes at moderate (6 wt % NaCl) concentrations of chlorides. Dots designate the same for gold. Arrows show T and pH variations in solutions for deposits of various genetic groups (numbers as in the table). Light solid lines depict acid high-chloride solutions (1–4); dash-and-dot lines, alkaline solutions (5–7, early stages); dashed lines, low-chloride sulfide solutions (8, 9).
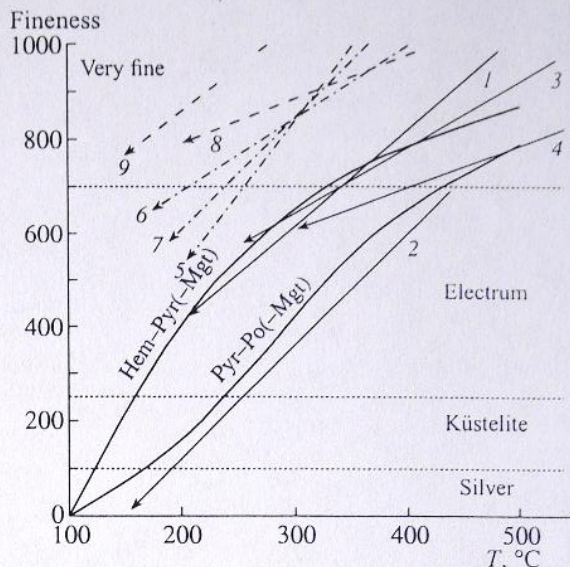

Fig. 2. Trends of fineness variation of native gold vs. temperature for deposits of different genetic types (arrows 1–9). The figure also shows possible limit compositions of Au–Ag alloys in equilibrium with Ag_2S for Hem–Pyr(–Mgt) and Pyr–Po(–Mgt) buffers (lines). Arrows show gold fineness variation with temperature for deposits of various genetic groups (legend as in Fig. 1).

perature range. Domain III is narrow and represents an environment promoting the formation of $Au(HS)_2^-$ (instead of gold monohydrosulfide) at high temperatures, although $AgCl_2^-$ remains stable even under pyrite–pyrrhotite buffer conditions. Conditions of the occurrence of Au and Ag as dihydrosulfide or monohydrosulfide complexes are depicted in domains IV and V. The arrows in Fig. 1 show the directions of the assumed evolution of T–pH parameters of solutions during the formation of nine genetic groups of gold deposits presented in the table (based on published data [2–4, 14, 15, and others]).

The initial stages of the formation of productive associations in epithermal alunite–quartz deposits with Au and Ag (genetic group 1) are represented by type I solution with high chloride contents, oxidative environment, and hyperacid pH values grading into subneutral values (domain II) at lower temperatures. The early productive stage in epithermal adular–quartz deposits (group 2) is also characterized by type I solution. However, it is more reductive, less acid, and transferred to the alkaline region (domain IV). Ores of genetic groups 1 and 2 are characterized by low Au/Ag ratios, wide variation of native gold fineness, and diversity of silver phases (sulfides, sulfosalts, and others). Similar physicochemical variation trends are also observed in porphyry gold–copper (group 3) and skarn gold (group 4)

deposits. Early generations of native gold in gold–telluride, gold–arsenic, and gold–antimony deposits (groups 5–7) may be accompanied by the transition of alkaline solutions at early stages (type IV) to subneutral solutions (type II) at later stages. Transitions from the primary alkaline (type IV) or subneutral (type V) to low-acid and low-chloride low-temperature conditions (V and II) are typical of gold deposits in Precambrian greenstone belts (8) and terrigenous–carbonate formations of the Carlin type (9), respectively. Ore deposits of genetic groups 8 and 9 are marked by high values of gold fineness and Au/Ag ratio and absence of silver sulfides.

Figure 2 depicts the inferred physicochemical settings of Au–Ag transport and deposition in different genetic groups of ore deposits. It shows compositions of native gold in equilibrium with Ag_2S in Ag-rich (arrows 1–4) and Ag-free (arrows 5–9) systems. Gold fineness can be used as a geothermometer, because the presence of silver sulfides in paragenetic associations reduces the system variance. Figure 2 shows the possible limiting compositions of Au–Ag alloys in equilibrium with Ag_2S for Hem–Pyr(–Mgt) buffer conditions are close to trends of native gold fineness in epithermal alunite–quartz (1) and porphyry gold–copper (3) deposits characterized by oxidizing conditions. Trends for epithermal adular–quartz (2) and gold–skarn (4) deposits are close to the reducing Pyr–Po(–Mgt) buffer. The dotted arrows in the upper part show the direction and limit of gold quality degradation in deposits with a low content of silver sulfides (arrows 8 and 9). Similar qualitative variations are typical of early (very fine) gold in

gold–telluride, gold–arsenic, and gold–antimony deposits (arrows 5–7).

Thus, comparison of thermodynamic modeling data and mineralogical–geochemical trends in the formation of gold deposits suggest that our analytical method may be used for the processing of logic-mathematical data and the quantitative simulation of comprehensively investigated natural objects of great importance.

REFERENCES

1. V. V. Shcherbina, Geokhimiya, No. 3, 56 (1956) [in Russian].
2. Yu. G. Safonov, Geol. Rudn. Mestorozhd., No. 1, 25 (1997) [Geol. Ore. Deposits, No.1, 20 (1997)].
3. M. M. Konstantinov, E. M. Nekrasov, A. A. Sidorov, et al., Giant Gold Deposits in Russia and the World (Nachnyĭ Mir, Moscow, 2000) [in Russian].
4. A. N. Nekrasov, V. Yu. Oreshin, and I. A. Chizhova, Rudy Metally, No. 5, 33 (1997).
5. G. W. Morrison, W. J. Rose, and S. Jareith, Ore Geol. Rev. 6, 333 (1991).
6. C. H. Gammons and A. E. Williams-Jones, Econ. Geol. 95, 420 (1995).
7. G. R. Kolonin, O. L. Gas'kova, and G. A. Pal'yanova, Geol. Geofiz., No. 7, 133 (1986).
8. G. R. Kolonin and G. A. Pal'yanova, Dokl. Akad. Nauk 373, 527 (2000) [Dokl. Earth Sci., 373, 1000 (2000)].
9. L. G. Benning and T. M. Seward, Geochim. Cosmochi. Acta 60, 1849 (1996).
10. A. Stefansson and T. M. Seward, Geochim. Cosmochi. Acta 67, 1395 (2003).
11. N. N. Akinfiev and A. V. Zotov, Geokhimiya, No. 10, 1083 (2001) [Geochem. Int., No. 10, 990 (2001)].
12. G. A. Pal'yanova and V. A. Drebushchak, Geokhimiya, No. 12, 1352 (2002) [Geochem. Int., No. 12, 1222 (2002)].
13. Yu. V. Shvarov, Geokhimiya, No. 6, 646 (1999) [Geochem. Int., No. 10, 571 (1999)].
14. D. I. Groves, R. J. Goldfarb, M. Gebre-Mariam, et al., Ore Geol. Rev., No. 13, 7 (1998).
15. Metasomatism and Metasomatic Rocks, Ed. by V. A. Zharikov and V. A. Rusinov (Nauchnyi Mir, Moscow, 1998).