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Forming conditions for Au-Sb and Ag-Sb ore according to thermodynamic modeling data

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Ore forming conditions for Au-Sb and Ag-Sb deposits have been estimated using thermodynamic modeling. PTX-parameters of ore-forming fluids obtained by fluid inclusion study in the minerals were used as original data for modeling. Analysis of composition of fluid inclusion solutions in the minerals of Au-Sb deposits together with mineralogical and geochemical data show that Au-Sb deposits were formed by two types of solutions: neutral–weak alkaline ($C_{Cl} < 5$ wt % NaCl-eq.), and acid high concentrated chloride solution (up to 30 wt% NaCl-eq.), containing $FeCl_2$ and $CaCl_2$ besides NaCl. In low concentrated chloride solution Sb is transported as sulfide and hydroxide complexes, and Au and Ag as bihydrosulfide species. In acid high chloride solution of late superimposed stage, which contains Cu, Ag, Pb, and Zn, predominating Au and Ag species are chloride complexes, and for Sb chloride and hydroxy-complexes. The main factors determining geochemical specialization of Ag-Sb ore are high chloride concentration and pH = 3.5–4, determining low Au-bearing capacity of the solution. Unsaturated in Ag low concentrated chloride solutions took part in Au-Sb deposit forming that determines their specific composition.

1. Introduction

Au-Sb and Ag-Sb vein hydrothermal deposits are known in nature. Which factors determine geochemical specialization of ore deposits in gold or silver: does it depend on specialization of ore-forming solutions or physicochemical conditions of ore-forming process? We try to answer this question using thermodynamic computer modeling in combination with mineralogical and geochemical data and fluid inclusion study.

2. General description of Au-Sb and Ag-Sb deposits

Au-Sb vein mineralization is commonly localized in regionally metamorphosed graphitized rocks and spatially removed from magmatic bodies, although granitoid intrusions occur in some ore districts. The deposits are characterized by simple mineral composition: quartz-stibnite veins with minor pyrite, arsenopyrite, bertierite, gold, carbonates, and rare aurostibite, sulfides and sulfosalts of Cu, Pb, Zn. Hydrothermally altered host rock (beresite) is composed of quartz, dolomite, ankerite, sericite, chlorite, pyrite, arsenopyrite, and graphite. Hydrothermal alteration was accompanied by input of CO_2, Fe, Mg, K, Ca, S, As, Sb. Au/Ag ratio in the ores varies from 5/1 up to 15/1.

Ag-Sb deposits are regarded as important industrial type of silver deposits, which is distinguished by high Ag contents (100-n 1000 ppm) and large reserves. Ag-Sb deposits are represented by quartz-siderite veins and vein zones in hydrothermally altered graphitizated terrigenous rocks near intruding them granite bodies and sometimes in granites. Main ore minerals are Ag-tetrahedrite, chalcopyrite and sulfosalts (chalcostibite, bournonite, zinkenite, jamsonite) with minor galena, pyrite and arsenopyrite and other sulfides. Au/Ag ratio ranges from 0.00001 up to 0.01.

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3. Composition of Au-Sb and Ag-Sb ores

Geochemical and mineral composition.
Two types of hydrothermal vein deposits are known: Au-Sb and Ag-Sb, which are characterized by a similar set of ore elements (Sb, As, Fe, Au, Ag, Cu, Pb, Zn) entering the ore composition in different quantities. The predominant elements in the Au-Sb deposits represent the following row: Sb, As, Fe, Au (± Cu, Pb, Zn). The Ag-Sb ore contains significant quantities of Sb, Cu, Fe, As, Ag, Pb, and Zn in the order of decreasing. Stibnite is a major mineral of Au-Sb deposits, and Sb-sulfosalts are minor and rare minerals. Sb-sulfosalts predominate in the ore of Ag-Sb deposits, and stibnite is the minor or rare mineral.

Gold content. There is no native gold in the Ag-Sb ore. Gold contents in the ore of Au-Sb deposits range from 1 up to n10 ppm. Native gold of high fineness (910–990) occurs mainly in arsenopyrite and pyrite. Low fineness gold (500–900) sometimes appears in the ore along with a Au/Ag ratio decrease at later stages of the hydrothermal process.

Deposition sequence of Au-Sb ore. Sequence of mineral deposition at Au-Sb deposits includes two main parageneses: 1) pyrite-arsenopyrite (main Au-bearing), and 2) stibnite ± bertierite, galena, tetrahedrite, Cu-Pb sulfosalts, at that mineral sequence starts with galena and finishes with stibnite crystallization. Sometimes parageneses of sulfide-sulfosalt stage (plagionite, chalcostibite, jamsonite, tetrahedrite, boulangerite, galena) are superimposed on stibnite veins and relate to the later second stage of hydrothermal mineralization.

Fluid inclusion study. Analysis of mineral parageneses of the ores and a sequence of their crystallization as well as fluid inclusion study allow us to obtain the preliminary data for modeling and the factors, having an affect on gold contents in Au-Sb ore and specific mineral composition. Fluid inclusion study indicates that the ores of Au-Sb and Ag-Sb deposits formed at a similar temperature ($<300^\circ$C) from the solutions of principally different composition. Ore-forming fluid of Au-Sb deposits represents low concentrated chloride solution (<5–9% NaCl-eqv.) and gas phase rich in CO_2. Lower contents of methane and nitrogen occur in gas phase. Minerals of pyrite-arsenopyrite and quartz-stibnite mineral parageneses of Au-Sb deposits crystallized from low chloride neutral - weak alkaline solution. Minerals of sulfide-sulfosalt stage, superimposed on quartz-stibnite veins, deposited from acid chloride solution with concentration of about 30% NaCl-eqv. (Uderey, Yenisei range; West Gore, Meguma, Canada; Wiluna, Australia) [1–3]. Similar acid high chloride solutions are typical for sulfide-sulfosalt ore of Ag-Sb deposits [4–6]. The solutions of Ag-Sb deposits are distinguished by high chloride concentrations (up to 38% NaCl-eqv.) and complex salt composition ($NaCl>FeCl_2>CaCl_2>KCl$). In gas phase CO_2, CH_4 and N_2 predominate. Important physico-chemical factors are temperature, composition and concentration of salt components of ore-forming solutions, and evolution of redox potential.

4. Computer thermodynamic modeling

To estimate a possible metal-bearing capacity of the hydrothermal solutions and to study the reasons of their geochemical specialization, computer modeling was performed using "Selektor" program based on the principle of free Gibbs energy minimization [7] and "Chiller" program [8] for multiphase chemical equilibrium calculation using equilibrium constants. Because only low concentrated solutions have been considered as possible Sb transport agents due to examples of stibnite deposition by hot springs, it was accepted by many authors that chloride complexes don't appear to play a role in hydrothermal Sb transfer [9–11]. Results of the study of EXAFS-spectra of $SbCl_3$-containing aqueous solution by Oelkers and co-authors show the presence of $SbCl_n$ species in the solutions at the temperature ranging from 25 up to 250 C [12]. Free Gibbs energies for chloride, hydroxy- and mixed hydroxy-chloride antimony species are calculated from stability constants of the reactions [13,14] using equation

$$\Delta G^0(T) = -2.303\, RT \text{ lgK} \tag{1}$$

for the each of species. These values, adapted to the SUPCRT database, are presented in Table I. ΔG^0 of antimony chloride species are based on stability constants, measured by Ovchinnikov and co-authors [15]. Zotov, Shikina and Akinfiev [11] have derived HKF equation parameters and estimated thermodynamic properties of antimony hydroxide specie based on their experimental data. Using their data we have obtained new results, which show a significant role of chloride and hydroxide antimony species in the hydrothermal solutions (Figs 1–3). Thermodynamic data for native antimony and sulfide antimony spices are taken from [16], and for stibnite and $Sb(OH)_3{}^0$ spice—from [11]. Standard thermodynamic data for varieties of the Au-Ag system are borrowed from [17], and for $AuHS^0$ and $AgHS^0$ spices—from [18, 19]. To reconstruct (with some degree of approximation) ore-forming process we used model of flow reactor and model of mineral deposition from the solution of adjusted composition during TP-parameter decrease. Flow reactor model is applicable for modeling of ore process in upper and peripheral parts of the ore-forming system, where fluid cools gradually in ore deposition zone without input of additional portions of the solution. Precipitation from the solution of adjusted composition is applied for the modeling of Ag-Sb deposits (on the example of Askhatin deposit [20], where in the structure

TABLE I $\Delta G_T{}^0$ (cal/mol) for chloride, hydroxide and mixed hydroxy-chloride Sb species and minerals

T°C	25	50	100	150	200	250
Tetrahedrite $Cu_{12}Sb_4S_{13}$	−208370	−204035	−214280	−217377	−219823	−211150
Chalcostibite $CuSbS_2$	−29672	−28896	−30250	−30510	−30667	−29114
$SbCl^{+2}$	−21300	−21350	−23990	−26450	−28920	−31800
$SbCl^{2+}$	−52000	−52520	−56130	−59810	−63550	−68150
$SbCl_3{}^0$	−82600	−83590	−88070	−93270	−98680	−104990
$SbCl_4$	−113500	−115250	−121100	−126600	−132011	−136730
$Sb(OH)_2{}^+$	−98700	−99400	−100900	−102710	−104620	−106810
$Sb(OH)_3{}^0$	−154100	−155210	−157870	−160620	−163930	−167180
$SbCl(OH)_2{}^0$	−131058	−132220	−136530	−139740	−144050	−148590
$SbCl_3OH^-$	−137256	−139330	−143990	−148620	−152930	−156680
$SbCl_2OH^0$	−106305	−107490	−110990	−115240	−119810	−125080
$SbCl(OH)_3$	−171460	−172520	−176100	−179530	−183070	−187210
$SbClOH^+$	−75760	−76390	−79010	−81850	−84740	−88230
SbS_2	−7400	−7960	−8910	−9520	−10060	−10300

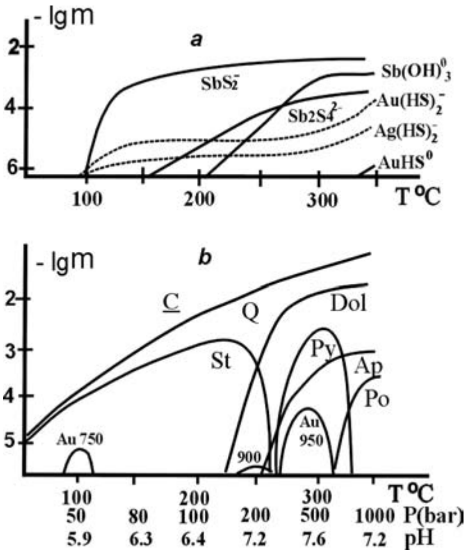

Figure 1 Au, Ag, and Sb species concentrations in 1 m NaCl solution (a), and sequence of mineral deposition at the PTX-parameters decrease (b). Start concentrations: m Sb = 0.005, Au/Ag = 5. Abbreviations: Po-pyrrhotite, Ap-arsenopyrite, Py-pyrite, St-stibnite, Dol-dolomite, Q-quartz, Au-native gold, C-graphite (phase in abundance).

of diverging array of veins (like "horse tail") mineral parageneses of different composition deposits at the different depth. Vertical zonation of Ag-Sb mineralization is similar to the lateral one: siderite-tetrahedrite veins change by siderite-chalcopyrite with pyrrhotite veins at below ore level. Models of flow reactor and model of adjusted composition are extreme cases of realization of ore-forming process. Some natural depositional processes includes combination of these two models. Ore-forming conditions are reconstructed for Au-Sb and Ag-Sb deposits based on calculated mineral deposition sequence, corresponding to observed in the ore. Modeling allow to estimate initial Au and Ag concentrations in the ore-forming solutions (acidic and neutral-weak alkaline) in the environment closely approximated to the natural conditions. Model solution compositions are based on mineralogical and geochemical data about the ore composition and hydrothermally altered rocks, and fluid inclusion study results. Aqueous phase of model solution of Au-Sb deposits contains 1 m NaCl and products of hydrolysis reactions, which were formed during an interaction of the solution with host rocks—small quantities of Ca, K, Mg, Fe, Si. Concentration of Au $5{\cdot}10^{-5}$ m, Ag $1{\cdot}10^{-5}$ m, and Sb $5{\cdot}10^{-3}$ m in the solution correspond to the Au/Ag/Sb ratio in the ore. The gas phase contains carbon dioxide, methane and nitrogen in ratio 2/1/0.1 Using Selektor

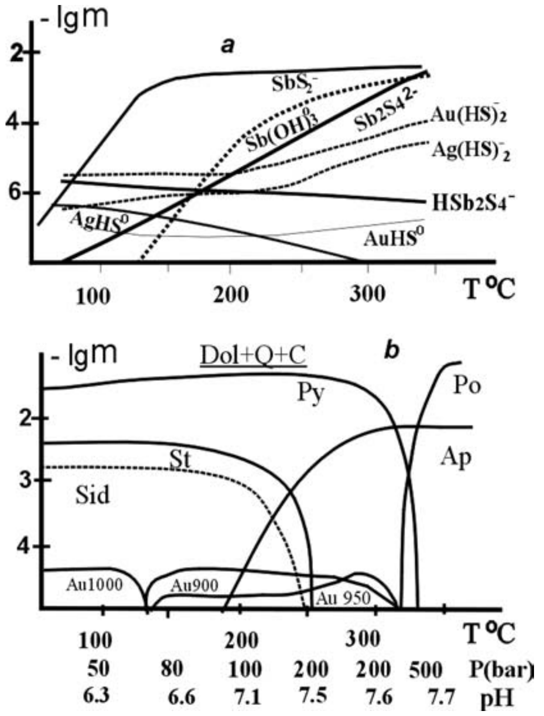

Figure 2 Au, Ag and Sb concentrations in 1 m NaCl solution (a), and mineral deposition sequence at the TP decrease (b). mSb = 0.005, Au/Ag = 5. Abbreviations: see Fig. 1. Phases in abundance are underlined.

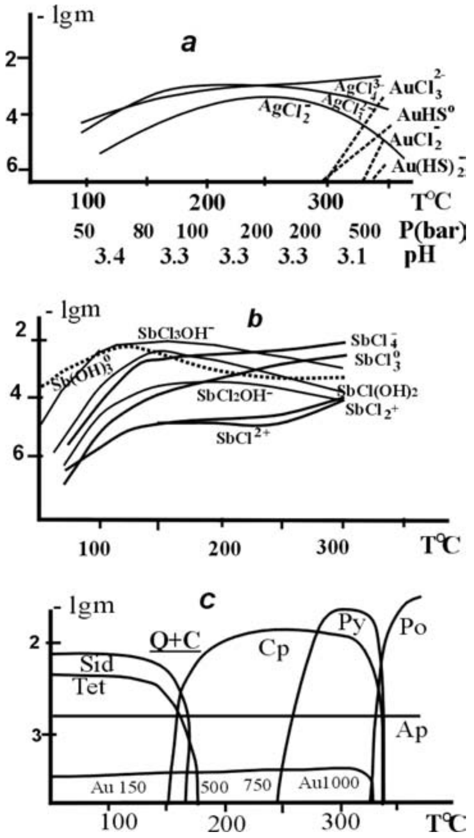

Figure 3 Au, Ag and Sb concnentrations in acid chloride 5 m solution at initial pH = 3.1 (a, b), and mineral deposition at the TP decrease (c). mSb = 0.024, Au/Ag = 0.1, Fe/Ca = 3/1. Abbreviations: see Figs I, 2.

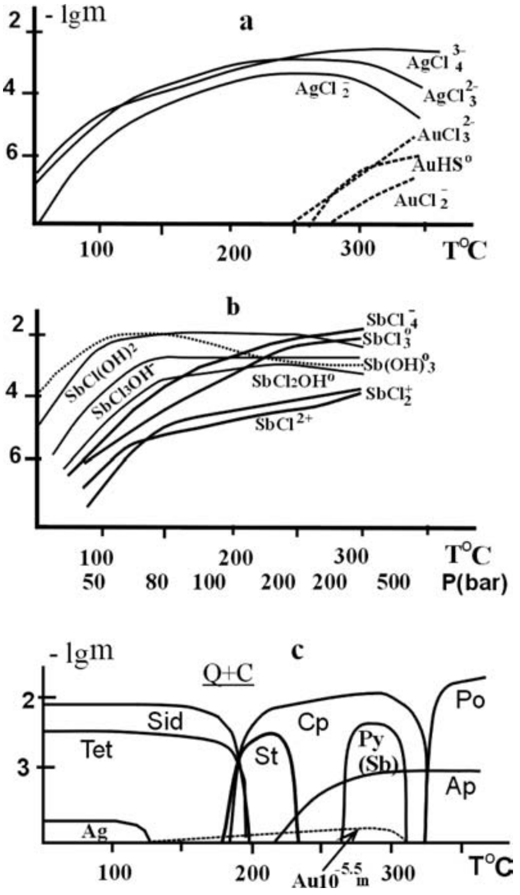

Figure 4 Ag, Au (a) and Sb (b) concentrations in the 5 m solution at pH = 3.5, and mineral deposition at the TP decrease (c). mSb = 0.024, Au/Ag = 0.1, Fe/Ca−1/3. Abbreviations: Tet-tetrahedrite, Cp-chalcopyrite, Sid-siderite, Sb-native Sb, other minerals—see Fig. 1. Phases in abundance are underlined.

program, flow reactor model shows that at the temperature decrease below 350°C pyrrhotite and arsenopyrite precipitate from the solution, then quartz, dolomite, pyrite, and native gold of high fineness (Fig. 1). Desulfidation of fluid due to wall-rock reaction promote Au precipitation from the solution. Most part of gold precipitates as native gold of high fineness (950), and about of $1 \cdot 10^{-5}$ m remains in the solution as hydrosulfide species down to low temperatures. Quartz-stibnite veins crystallize at the temperature below 250°C with insignificant quantity of low fineness gold at a temperature of 100°C.

In the case of ore deposition from the fluid of adjusted composition in the fissures under ramp-down temperature and pressure (Fig. 2, Selektor program) high fineness gold only occurs in the ore together with stibnite. If the concentration of sulfide sulfur does not decrease with cooling, gold solubility remains sufficiently high, and gold may occur in the solution as hydrosulfide species down to low temperatures.

Figs 3 and 4 describe how TP-change affects metal complexing and mineral solubility at the Ag-Sb deposits using model of adjusted composition (Selektor program). TP-parameter decrease results in pH and redox potential (Eh) alteration.

Pyrite and arsenopyrite which crystallized at the first stage of mineral deposition both in the Au-Sb and Ag-Sb deposits are the characteristic minerals indicating sulfide sulfur concentration of about 10^{-1} m [21]. Following sulfosalt paragenesis indicates sulfide sulfur concentration decrease. So, at the temperature $\geq$ 300 °C common sulfide sulfur concentration is about 10^{-1} m, and at the $T < 250$ °C 10^{-2} m. Fig. 4 demonstrates results of modeling of Ag-Sb mineralization forming from the 5 m chloride solution, containing 2.6 m NaCl, 0.75 m $CaCl_2$, 0.25 m $FeCl_2$ and 0.2 m $MgCl_2$. Gas phase contains carbon dioxide, methane and nitrogen in ratio 2/1/0.01. Mineral phases deposited from the solution, and sequence of their precipitation correspond to those observed in the ore: higher temperature association of Fe and Cu sulfides change by lower temperature siderite-tetrahedrite paragenesis, at that minor stibnite crystallizes before Ag-containing tetrahedrite. Model of flow reactor ("Chiller" program) demonstrates similar results (Fig. 5), taking in account reactions with the participation of sulfosalts, such as pyrargyrite and polybasite.

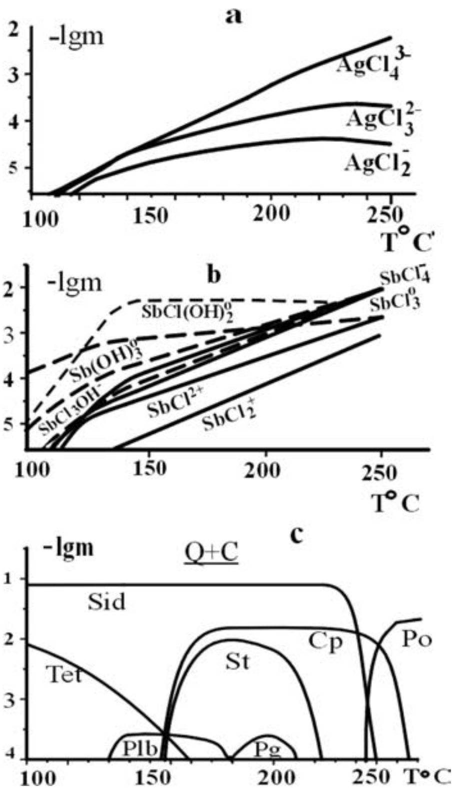

Figure 5 Deposition of Ag and Sb phases from 4 m chloride solution (a), concentrations of Sb species in the solution (b), and concentrations of Ag species (c). Abbreviations: Plb-polybasite, Pg-pyrargyrite, other minerals—see Figs 1 and 2.

5. Estimation of metal-bearing capacity of the ore-forming solutions

Low concentrated chloride or chloride-carbonate fluid of first stage of Au-Sb deposits at 350°C is characterized by following parameters: pH 7.7 – 7.2, Eh $= \sim -0.5$ v, start common concentration of sulfide sulfur of about 0.11 m (Fig. 1). Calculated Ag solubility in such a solution is about 10^{-4} m that coincides with the data, experimentally obtained by Sugaki and co-authors [22]. Au solubility in near neutral - weak alkaline aqueous phase of ore-forming fluid is about 10^{-4} m (up to $10^{-3.6}$ m by experimental data of A. Stefansson and T. Seward [23]) that similar to Ag solubility, and then Au/Ag ratio in the solution must correspond to 1/1. Gold and silver in such a solution could be transported mainly as hydrosulfide $Au(HS)_2{}^-$ and $Ag(HS)_2{}^-$ species, and antimony as sulfide and hydroxy-complexes. Cooling of such solution results in deposition of low fineness gold (700–650) only in the association with stibnite. However, low fineness gold is not a characteristic feature for Au-Sb ore, on the contrary, high fineness gold predominates in the ore (950). High fineness gold deposits from such a solution at Au/Ag = 5/1 (Fig. 1, 2), as really occurs in Au-Sb deposits (15/1−5/1). It's suggests that Ag unsaturated ore-forming fluids took part in forming of Au-Sb deposits, that determine their geochemical specialization and conditions of fluid generation in magmatic center.

Superimposition of sulfide-sulfosalt stage on quartz-stibnite veins gives rise to recrystallization and partial redeposition of ore matter. Interaction of high chloride solution with pyrite and stibnite results in pH decrease to 3.1 and gold remobilization. Redeposited gold is characterized by low fineness (Fig. 3). Low temperature associations contains Au-containing silver.

Modeling results show that highly concentrated chloride solutions of Ag-Sb deposits at the temperature 350°C and pressure 200 bar in equilibrium with carboniferous shales (typical host rock for Ag-Sb deposits) are characterized by following thermodynamic parameters: pH $=$ 3.5–4, Eh $= -0.2$ v, and common sulfide sulfur concentration ~ 0.05 m [6]. The element contents in such solution reach up to 10^{-2} m Ag, 10^{-2} m Sb, and 10^{-5} m Au, predominating Au and Ag species are chloride complexes, and for Sb chloride and hydroxy-complexes (Fig. 4). So, this solution specializes mainly in Ag and Sb, and deposited mineral parageneses of Ag-Sb ore at the temperature decrease (siderite, tetrahedrite, chalcopyrite, etc.) do not contain native gold. Native antimony appears in mineral paragenesis instead of pyrite at lower concentrations of sulfide sulfur and a redox potential decrease, therefore Sb is shown in parenthesis in Fig. 4.

High acid chloride solutions (pH = 3) potentially could transport greater Au quantities up to $10^{-3.5}$m, Sb up to 10^{-2}m, and Ag up to $10^{-1.5}$m, predominantly as chloride ($AuCl_3{}^2$, $AuCl_{2-}$, $AgCl_4{}^{3-}$, $AgCl_3{}^{2-}$, $AgCl_{2-}$, $SbCl_{4-}$, $SbCl_3{}^\circ$, $SbCl^{2+}$, $SbCl^{2+}$), $AuHS^\circ$ and $Sb(OH)_3$ species (Fig. 3). At a temperature decrease, high fineness gold deposits at T 300°C, electrum at T<250, and Au-containing silver (or kustelite) at 100°C, that is characteristic feature of Au-Ag deposits. Because Au is not indicated in the ore of Ag-Sb deposits, which formed at temperature range from 280 down to 100°C, consequently, there was no gold in the ore-forming solutions at 350–300°C. The low gold-bearing capacity of high chloride solution or low value of Au/Ag ratio (<0.01) could exist only at the pH range 3.5–4.5 at the same value of redox-potential. Therefore, the main factors, determining geochemical specialization of Ag-Sb ore, are a high chlorine concentration and pH value of about 4.

6. Conclusions

Our performed research shows that sharp distinctions in Au/Ag ratios in the different ore types (Au-Sb, Ag-Sb, Au-Ag) are not determined by physico-chemical conditions of their formation alone, but also by the specialization of ore fluids, forming at the level of fluid-generating center. Likely, low Au-bearing capacity of silver-arsenide (Ni-Co-Ag-Bi-U) deposits and sharp variations of Ag content in the gold deposits of different types could be explained by these reasons. New approach to the modeling of gold and silver bearing systems allow to determine factors of forming of different ore types in the environment close to natural conditions and obtain quantitative characteristics of gold and silver joint deposition.

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