

POSSIBILITIES OF EXPERIMENTAL CALCULATION METHOD ON PREDICTION FORMS OF GOLD IN SULFIDES

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For conditions of hydrothermal sulfide formation a computer modelling of the gold concentration processes has been first performed with an additional account of adsorptive equilibria. The results of our experiments on gold dissolution and its precipitation on pyrite in sulfide chloride acid solutions at $t=200$ and 250°C were used to the basic data [1]. The conception of Sahai and Sverjensky [2] was accepted as a thermodynamic foundation for the variant of existence on the sorbent surface of single-position and energy equivalent vacancies for formation of a surface complex of the specified stoichiometry.

According to this methodology a version of transition from experimentally studied equilibrium $\text{Au}_{(\text{solution})} \leftrightarrow \text{Au}_{(\equiv\text{FeS}_2)}$ with the coefficient of total gold distribution between pyrite and solution $K_D = C_{\text{Au}(\equiv\text{FeS}_2)} / C_{\text{Au}(\text{solution})}$ to adsorptive equilibrium $\equiv\text{FeS}_2 + \text{Au}(\text{HS})^\circ \leftrightarrow \equiv\text{FeS}_2 \cdot \text{Au}(\text{HS})$ was suggested with an apparent constant $K_A = m_{\equiv\text{FeS}_2 \cdot \text{Au}(\text{HS})} / m_{\text{Au}(\text{HS})^\circ} m_{\equiv\text{FeS}_2}$. Concentration of $\text{Au}(\text{HS})^\circ$ was calculated on the basis of experimental data for the total content of the dissolved gold as well as for its share in the summary balance $\text{Au}(\text{HS})^\circ + \text{Au}(\text{HS})_2^-$ for acid H_2S -containing solutions (basis of thermodynamic data UNITHERM, program package HCh [3]).

The composition of the surface complex $\equiv\text{FeS}_2 \cdot \text{Au}(\text{HS})$ corresponded to a hypothetical one, but not to inconsistent ideas about mechanism of gold consolidation on pyrite surface [4, 5]. Moreover, the nonmetallic state of reprecipitated gold in conditions of our experiment was determined by spectroscopic methods [6]. The equilibrium component $\equiv\text{FeS}_2$ is a formal parameter that means a quantity of vacancies on the pyrite surface area. In accordance with the instrument of description of adsorptive equilibria, concentrations of all compounds are accepted in molality scale. The formally taken values $m_{\equiv\text{FeS}_2}$ were consistent with values 1, 2, 4 m in direct proportion with the pyrite content (8, 16 and 32 g $\text{FeS}_2 / 1 \text{ kg H}_2\text{O}$). The values of the constant obtained for adsorptive equilibrium K_D and K_A for temperatures 200 and 250°C are given in Table 1.

Table 1

Values K_D and K_A of the pyrite-solution equilibrium for 200 and 250°C for the following conditions of experiment: $m_{\text{H}_2\text{S}} = 0.1$; $m_{\text{NaCl}} = 0.17$; $m_{\text{S}_8(\text{solution})} = n \cdot 10^{-4}$; pH 3.8; FeS_2 , g / 1 kg $\text{H}_2\text{O} = 8 \div 32$; $\text{Au}_{(\text{met})}$ - an excess

$K_D = C_{\text{Au}(\equiv\text{FeS}_2)} / C_{\text{Au}(\text{p-p})}$				
t, °C	$C_{\text{Au}(\equiv\text{FeS}_2)}$, ppm	$C_{\text{Au}(\text{p-p})}$, ppm	$m_{\equiv\text{FeS}_2}$	K_D
200	126	6.1	-	20 ± 10
250	500	6.0	-	80 ± 20
$K_A = m_{\equiv\text{FeS}_2 \cdot \text{Au}(\text{HS})} / m_{\equiv\text{FeS}_2} m_{\text{Au}(\text{HS})^\circ}$				
t, °C	$m_{\equiv\text{FeS}_2 \cdot \text{Au}(\text{HS})}$	$m_{\text{Au}(\text{HS})^\circ}$	$m_{\equiv\text{FeS}_2}$	K_A
200	$5.12 \cdot 10^{-6}$	$3.85 \cdot 10^{-6}$	1	1.33
250	$2.03 \cdot 10^{-5}$	$1.71 \cdot 10^{-5}$	1	1.19

Note: The concrete value of K_A is given for the experiment with pyrite content 8 g / 1 kg H_2O ($m_{\equiv\text{FeS}_2} = 1$)

Next, through values of K_A obtained free energies of adsorptive complex were calculated according to the equation $G_{\equiv\text{FeS}_2 \cdot \text{Au}(\text{HS})}^\circ = -RT \ln K_A + G_{\text{Au}(\text{HS})^\circ}^\circ + G_{\equiv\text{FeS}_2}^\circ$, the values of $G_{\equiv\text{FeS}_2}^\circ$ functional group of positions $\equiv\text{FeS}_2$ being taken as equal to a zero value for all temperatures. Prepared in such way values of $G_{\equiv\text{FeS}_2 \cdot \text{Au}(\text{HS})}^\circ$ turned out to be equal to 0.79 and -7.88 kJ/mol for 200 and 250°C , respectively.

The conditions of formation of sulfide structures in hydrothermal field Logachev (MAR) with simplified the constitution of system, including $\text{Au} + \text{FeS}_2 + \text{H}_2\text{S} + \text{NaCl} + \text{H}_2\text{O}$ were accepted as a prototype of the calculation gold concentration model in various forms. In addition, the specified quantity of the nitrogen in oxidized form (HNO_3) was considered, which was almost completely reduced to dissolved gas $\text{N}_2(\text{aq})$, as it had occurred in experiments with the measured oxidation of hydrogen sulfide [1]. The dissolved form of molecular sulfur $\text{S}_8(\text{aq})$ was chosen as an indicator of an oxidation degree of hydrogen sulfide and as a system compound for calculation of sulfur fugacity according to

equilibrium $S_8^{\circ}(aq) \leftrightarrow 4S_2(gas)$. Values of G° for $S_8^{\circ}(aq)$ in form of regressive equation HKF were obtained by processing of the data available as to solubility of elementary sulfur $S(el)$ [7, 8] in water. Initial system constitution: FeS_2 – from 8 to 320 g/kg H_2O ; Au – 9.25 and 7.1 mg/kg H_2O for 200 and 250°C, respectively; H_2S – 0.1m; NaCl – 0.17m; HNO_3 – from $1.56 \cdot 10^{-3}$ to 10^{-10} m.

Calculations for experimental conditions (Table 2) with minimal pyrite content (8 g/kg H_2O) and maximal oxidizer content ($m_{HNO_3} = 1.56 \cdot 10^{-3}$) in system composition were carried out as a rough approximation. According to data from the table, it is obvious that a profound redistribution of gold occurs between the solution and its precipitated forms Au(met) and Au(ads), besides with a great advantage in favour of surface complex (almost 100%). Predicted by calculation the contents of the adsorbed gold are close to experimental values for our experiments with an excess of Au(met): 159 ppm relative to 126 ppm for 200°C and 350 ppm relative to 500 ppm for 250°C (see fab. 1).

Table 2

The results of calculations of the solution constitutions and equilibrium to them contents of gold in pyrite in metallic Au(met) and adsorbed Au(ads) forms at $t=200$ and 250°C ($P=P_{psv}$) with content of FeS_2 equal 8 g/kg H_2O

$t, ^{\circ}C$	$m_{H_2S}, n \cdot 10^{-2}$	$m_{S_8^{\circ}}, n \cdot 10^{-4}$	$m_{Au(HS)^{\circ}}, n \cdot 10^{-5}$	$m_{Au(HS)_2^{\circ}}, n \cdot 10^{-5}$	pH	Au(met), ppm	Au(ads), ppm	Au(ads) / Au(total) · 100%
200	9.6	3.9	0.50	3.53	3.6	3.18	159	98.0
250	9.7	2.3	1.2	0.97	3.5	3.03	350	99.1

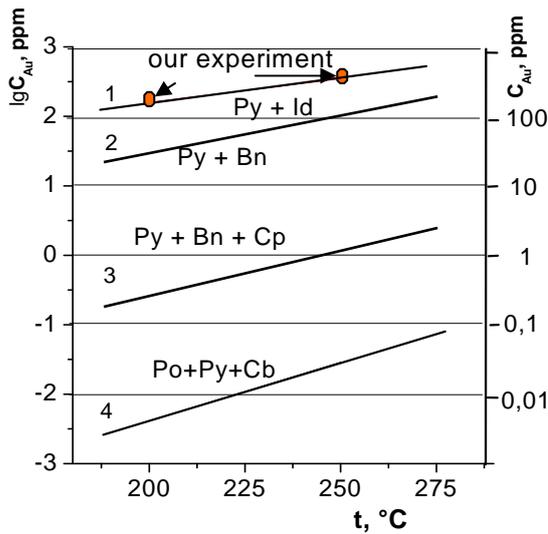


Fig.1. Calculated dependencies as to temperature influence on equilibrium contents of the adsorbed on pyrite form of gold in presence of Au(met) for various sulfide assemblages. Designations: Py – pyrite; Po – pyrrhotite; Cb – cubanite; Cp – chalcopyrite; Bn – bornite; Id – idaite.

Further calculations in the same system were performed with decrease of oxidizer quantities and reduction of sulfur fugacity down to values, corresponding to joint existence of pyrite with buffer assemblages idaite-bornite, bornite-chalcopyrite, chalcopyrite-cubanite-pyrrhotite according to [9]. According to the results of these calculations it has been established (fig. 1) that a considerable decrease of the predicted contents of the absorbed on pyrite gold must occur in the temperature interval 200 – 250°C at the decrease of sulfur fugacity for 0.1m solution H_2S .

Its maximal concentrations (more than 200 ppm) are consistent with the conditions of our experiment and field of the possible existence of idaite $Cu_5Fe_{-1}S_6$ (curve 1). The calculated contents of Au(ads) correspond to the interval 200 – 20 ppm with the transfer into the bornite stability field Cu_5FeS_4 (curve 2). Curve 3 with gold concentration 4 – 0.2 ppm turned out to correspond to a buffer pyrite-bornite-chalcopyrite assemblage. Negligible gold contents (< 0.1 ppm) are typical for conditions of existence of pyrite with pyrrhotite and cubanite (curve 4).

The position of isotherms (200 and 250°C) of the limited contents Au (ads) relative to sulfur fugacity (fig. 2) testifies to its substantially greater influence in comparison with the temperature factor. The most realistic for nature conditions of gold concentrations in «invisible» form (1 – 10 ppm) at these temperatures are consistent with the values of sulfur fugacity about 10^{-13} – 10^{-11} bar. At the stable

existence under these conditions of the pyrite-bornite assemblage, it is supposed to be more enriched in «invisible» gold in compared to assemblages, including pyrite, pyrrhotite, chalcopyrite, cubanite.

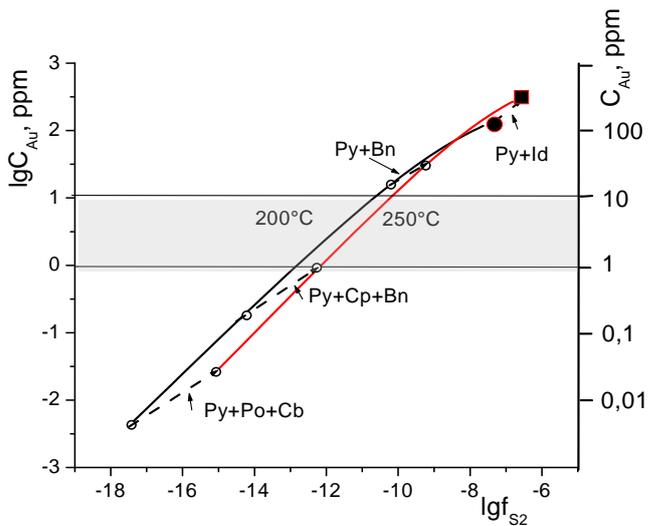


Fig.2. Calculated isothermal dependences of maximal concentrations of adsorbed on pyrite gold in the equilibrium with Au(met) on sulfur fugacity. Points f_{S_2} are plotted in the curves for equilibrium sulfide assemblages according to [9] and connecting them dashed lines for $t=200$ и 250°C . Area of the most real gold concentrations in pyrite– $1 \div 10$ ppm is darkened. Designations: Py – pyrite; Po – pyrrhotite; Cb – cubanite; Cp – chalcopyrite; Bn – bornite; Id - idaite

This regularity can be predicted in the case of the content change of sulfide aggregates in a cross-section of the big pipe of the black smoker Anna-Louise (Logachev field), as well as Rainbow structures [10], where a contrasting transition occurs from covellite to bornite with chalcopyrite and then to isocubanite in direction from an external to internal part. The decrease of sulfur fugacity in this row of sulfide assemblages (as a consequence of the reduction degree of oxidability of H_2S – containing solutions in the area of contact with sea water) must cause a reduction of the share of chemically connected «invisible» gold inside the internal zones of the oceanic structures.

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