

¹Baranova N.N., ²Tagirov B. R., and ²Zotov A.V. Experimental study of Au(HS)₂⁻ stability at 450°C and 1000 bars

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Available experimental data on Au_(cr) and Au₂S_(cr) solubility suggest that the thio complexes AuHS⁰ and Au(HS)₂⁻ are the main species responsible for the hydrothermal mobility of gold. A great deal of experimental work is devoted to the determination of stability of these species at subcritical temperatures (see, for example, Benning and Seward (1996) and references therein). However, very few data characterizing the hydrothermal mobility of gold at supercritical PT- parameters are available (Benning and Seward, 1996; Gibert et al., 1998; Louks and Mavrogenes, 1999; Fleet and Knipe, 2000). This fact is partially connected with the difficulties in controlling the parameters of the gold dissolution reaction in high temperature fluids. Therefore, the object of the present study is to determine the stability of Au(HS)₂⁻ at supercritical PT-parameters in the system with pH, hydrogen and sulfur fugacity reliably buffered by mineral assemblages.

EXPERIMENTAL. Natural low albite, nepheline and synthetic corundum, magnetite and pyrrhotite were used in the experiments. XRD patterns corresponded to the 9-466 ASTM card for albite, 35-424 for nepheline, 42-1468 for corundum, and 19-629 for magnetite. Solubility experiments were carried out at 450°C and 1000 bars in ~20 ml titanium autoclaves passivated with HNO₃. The temperature was measured with the accuracy ±2°C, and pressure was controlled by the degree of filling of the autoclaves according to the PVT data for H₂O-NaCl system (Potter and Brown, 1977). A mixture of the of silicate mineral

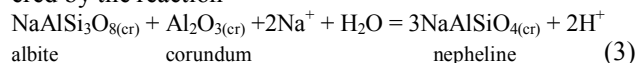
powders (about 1 g) was loaded into the autoclave together with aqueous solution. A mixture of pyrrhotite and magnetite powders (0.5 g of each mineral) was placed into a small titanium baker fixed together with the strip of 99.9% gold foil in the upper part of the autoclave. Therefore, pyrrhotite, magnetite and gold were allowed to react with the solution only under heating. About 50 mg of Al rod was loaded into each autoclave to generate hydrogen. The most of hydrogen escaped and reacted with pyrrhotite and magnetite and the autoclave walls during experiment so that the gold equilibrium concentration, which is connected with the hydrogen fugacity, was reached from undersaturation. Before the experiments argon was passed during 20 min. through the charged autoclaves to replace air, then the autoclaves were closed and placed into heated furnaces. Duration of the experiments was 8 days. Autoclaves were quenched slowly with cold air. Quench solutions were extracted and filtered through ~5µm filter. Then the autoclaves walls, together with the silicate minerals, were washed with the hot aqua regia, which was passed through the same filter and added to the quench solution. Gold was analyzed by atomic absorption spectroscopy. Solutions preparation method is described in details in Zotov et al. (1990). Presence of each mineral after experiment was verified via XRD.

RESULTS AND DISCUSSION. Experimental results are given in Table 1 together with the calculation of the reaction constant



$$\log K_1 = \log m(\text{Au}(\text{HS})_2^-) + 0.5\log f(\text{H}_{2(g)}) - \log m(\text{HS}^-) - \log m(\text{H}_2\text{S}_{(aq)}) \quad (2)$$

Alkaline pH of the experimental solutions were buffered by the reaction

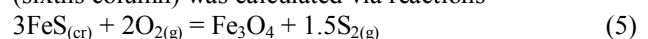


$$\log K_3 = 2\text{pNa} - 2\text{pH} \quad (4)$$

Table 1. Experimental results and calculation of the constants of reaction (1).

Measured:			Calculated:						
I	II	III	IV	V	VI	VII	VIII	IX	X
m(NaCl)	m(Au)·10 ⁶	d ₍₁₀₂₎ Å	N (FeS)	a (FeS)	log f(H ₂)	m(H ₂ S _{aq})·10 ²	m (HS ⁻)·10 ³	pH	log K ^o
0.1	6.7	2.071	0.955	0.696	0.13	1.38	8.73	8.00	-1.20
0.33	2.5	-	0.957	0.715	0.23	1.35	5.56	7.72	-1.36
0.33	3.8	2.072	0.957	0.715	0.23	1.35	5.56	7.72	-1.18
1	2.5	2.065	0.944	0.593	-0.42	1.45	4.06	7.72	-1.58
1	1.2	2.067	0.951	0.658	-0.07	1.26	3.54	7.46	-1.61
BLANK									
0.1	0.03								
1.0	0.03								
average log K ^o ₍₁₎ = -1.39±0.18									

Sulfur fugacity was controlled by the FeS activity in pyrrhotite. It was evaluated from the pyrrhotite d₍₁₀₂₎ spacing (Table 1, third column) using the data of Toulmin and Barton (1964). Hydrogen fugacity reported in Table 1 (sixths column) was calculated via reactions



and is slightly higher than the pyrite-pyrrhotite-magnetite equilibrium hydrogen pressure. Solute speciation calcula-

tions were performed with the help of GIBBS computer code (Shvarov and Bastrakov, 1999). Thermodynamic properties of aqueous species and pyrrhotite were taken from SUPCRT92 (Johnson et al., 1992), those for NaOH^o_(aq) from Shock et al. (1997), albite from Berman (1988) and Sverjensky et al. (1991), nepheline from Robie et al. (1978), and magnetite from Hemingway (1990). Calculated values of the logarithms of the reaction (1) constants are given in the last column of Table 1.

Fig.1. Measured gold concentration as a function of calculated pH_T

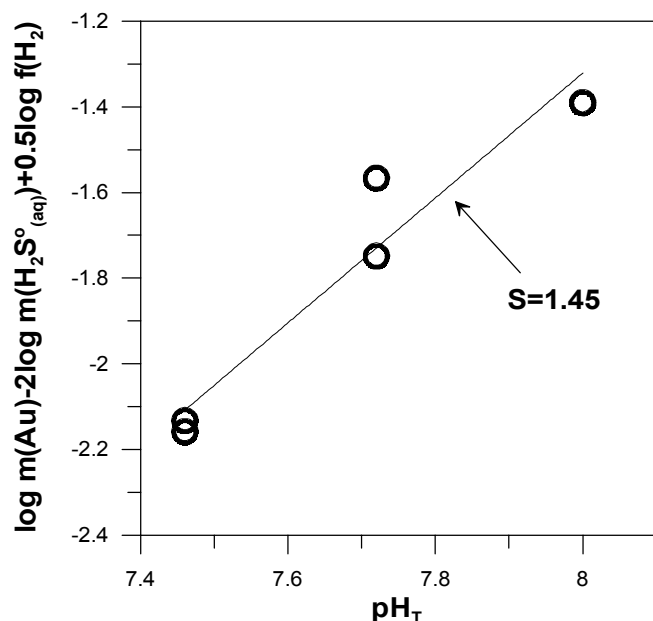
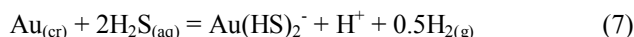


Figure 1 shows dependence of the Au concentration on the calculated pH. Measured gold concentration was corrected for the hydrogen fugacity and H₂S activity according to the reaction



The observed slope ($S=1.45$) is somewhat higher than the theoretical value $S = \frac{\partial \log a(\text{Au}(\text{HS})_2^-)}{\partial \text{pH}} = 1$ which is proba-

bly connected with the effect of activity coefficients and the errors in calculating hydrogen fugacity and pH. However, data plotted in Fig 1 imply that the charged gold complex predominates in experimental solutions. Calculated value of the reaction (1) constant is compared with the literature data in Fig. 2. This value agrees within ± 0.5 log unit with the prediction of Sverjensky et al. (1997) and extrapolation of the experimental data of Benning and Seward (1996).

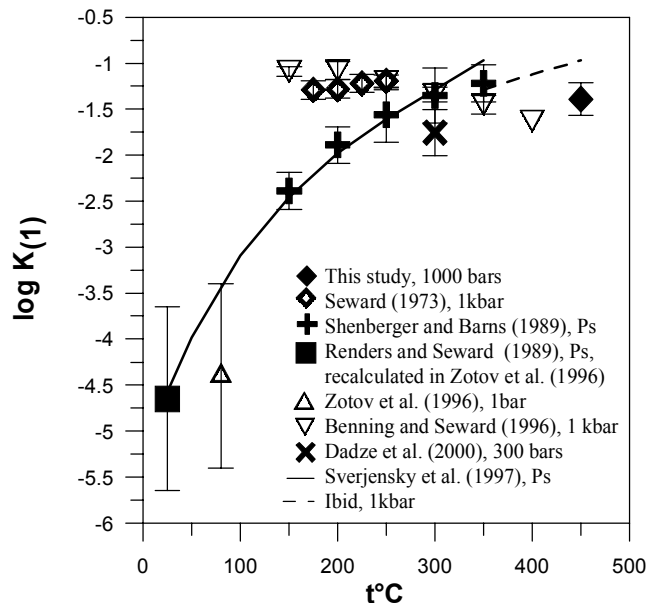
CONCLUSIONS. Gold solubility was studied in the system with pH, $a(\text{H}_2\text{S})$ and $f(\text{H}_2)$ controlled by the nephelin-albit-corundum and pyrrhotite-magnetite mineral assemblages at 450°C and 1000 bars. At these parameters $\log K = -1.39 \pm 0.18$ for the reaction $\text{Au}_{(\text{cr})} + \text{H}_2\text{S}_{(\text{aq})} + \text{HS}^- = \text{Au}(\text{HS})_2^- + 0.5\text{H}_{2(\text{g})}$. This value agrees within ± 0.5 log unit with the prediction of Sverjensky et al. (1997) and extrapolation of the experimental data of Benning and Seward (1996), that were obtained using a principally different experimental method.

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Fig.2. Logarithm of the reaction (1) constant as a function of temperature



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