GOLD SOLUBILITY IN CHLORIDE MEDIUM INTERACTED WITH EPIDOTE BEARING PROPYLITES

Likhoidov G.G., Plyusnina L.P., Scheka J.A.

(Far East Geological Institute, Vladivostok, Russia)

glikh@hotmail.com; fax: (4232) 31-78-47; phone (4232) 31-76-01

Many gold and polymettalic deposits are disposed within epidote propylites forming external zones of alteration. Preliminary experimental study of epidote stability in chloride solutions defined neutralization of both acid and alkaline solutions at their interaction [1]. The purpose of our study was to characterize the interaction of epidote propylites with gold bearing aqueous chloride solutions under hydrothermal conditions. In this paper we present results of gold solubility measurements at 300 and 400°C isotherms and P_{tot} = 1 kb in complex chloride-sulfide media buffered by the mineral associations of epidote propylites. Some thermodynamic calculations were also performed to determine "in situ" values of pH, and O_2 fugacity.

Hydrothermal experiments were performed in externally heated titanium alloy autoclaves using a furnace accurate to ±5°C. Internal pressure equal to 1kb was maintained by adding appropriate amounts of distilled water, in accord with P-V-T relations. Gold ampoules (9×80×0.2 mm) welded after charging served as the source of metal for solubility determination. The charge including starting solution along with a solid buffer mixture was placed into the same ampoule. Natural epidote, albite, calcite, and synthetic quartz, hematite, magnetite were used in runs to model a sulfur-less system. For modeling the sulfur-bearing media, natural pyrite was added to the mixture. The amount of each mineral phase was about 30mg. The volume of a starting solution (1mNaCl +0.001mNaOH, 1mNaCl, or 1mNaCl+0.001mHCl) was calculated in accordance with the P-V-T relations. Duration of the runs, defined by special kinetic series, varied from three weeks (at 300°C) to two weeks (at 400°C). Gold was extracted in dioctyl sulfide and analyzed by AAS with an accuracy of about 20%. X-rays were used to control the buffer end composition.

Relations between epidote–albite-calcite-quartz-hematite association and aqueous chloride solutions are described by the hydrolysis reaction: $Ep_{33} + 3Qtz + 2Na^+ + 2CO_2 + 0.5H_2O = 2Ab + 2Calc + 0.5Hem + 2H^+$ (1). Equilibrium of the reaction was initially ascertained at 200-350°C, 1kb in aqueous NaCl solutions of variable acidity [1]. In the 1mNaCl+0.001mNaOH solution at 360°C and over, newly formed hedenbergite (Hed) was noted. The Hed was identified by X-ray diffraction and microprobe analysis as $Ca_{0.92}Na_{0.06}Fe_{0.89}Al_{0.07}Si_{1.98}O_6$. The reaction (1) was used as a buffer of pH and oxygen fugacity for the study of gold solubility. At 300 and 400°C, the total Au concentration in quenched solutions was about (logmAu) -7.56±0.30 and -7.29±0.10, respectively (Tab. 1).

Table 1

Total gold content and pH in chilled solutions

Starting solution*	Ep-Qtz-Ab-Calc-Hem±Mgt			Ep-Qtz-Ab-Calc-Hem-Mgt-Py		
	logmAu	pH	N	logmAu	pH	N
300°C						
S1	-7.80	5.6	4	-6.78	5.1	4
S2	-7.67	6.4	3	-6.56	5.9	3
S3	-7.22	6.6	3	-6.56	6.0	3
AvM	-7.56	6.2	10	-5.54	5.7	10
AvC	-10.72	-	-	-4.28 (-6.49)	-	-
400°C						
S1	-7.40	6.3	4	-6.08	5.8	3
S2	-7.18	6.4	4	-6.20	6.3	3
AvM	-7.29	6.3	8	-6.14	6.0	6
AvC	-9.72 (-7.45)	-	-	-3.28	-	-
S3	-6.69	7.0	2	Hed appearance		

*S1 - 1mNaCl+10^{-3}mHCl, S2 - 1mNaCl, S3 - 1mNaCl+10^{-3}mNaOH; averages: AvM - measured, AvC - calculated by "Selector-C" [2], in parenthesis by "Gibbs" [3].

It must be noted that differences between logmAu values measured for different starting solutions on the isotherm are confined to uncertainty limits, and confirmed buffering capacity of the reaction (1). Some increase in Au content observed at 400°C with starting 1mNaCl+0.001mNaOH solution may be conditioned by the appearance of Hed and consequent instability of the reaction (1).

However in nature, epidote propylites, including gold mineralization, often contain sulfides. Sulfur plays a large part in mass transfer of gold because its hydrosulfide species are of great importance in gold dissolution [4]. In the presence of pyrite reaction (1) transforms to: $Ep_{33} + 3Qtz + 2Mgt + 2CO_2 + 2S_2 + 0.5H_2O + 2Na^+ = 2Ab + 2.5Hem + 2Py + 2Calc + O_2 + 2H^+$ (2). In runs with the assemblage (2), total Au solubility increases by 1-1.3 orders of magnitude in comparison with sulfur-less system that confirms the apparent role of Au hydrosulfide species in gold dissolution.

Thermodynamic calculations were performed to define gold speciation, pH and fo$_2$ values at T-P parameters of interest. The proportions of solids and solutions used in the calculations were analogous to those in runs. Basic data for solids, aqueous species and gases used in the calculation are embedded in the "Selector-C" [2] package data file SPR_98 – an updated version of SUPCRT92 [5]. Calculations were performed at 250, 300, 350, 400°C and 1 kb total pressure. In the presence of associations (1), oxygen fugacity vary in the range $–27.31 < logf_{O2} < -17,69$ at 250 and 400°C, respectively. The conditions are more oxidative in comparison with values peculiar to the HM buffer, which explains the magnetite instability observed in runs. The interaction of chloride solutions with the assemblage (2) leads to decrease in logfo$_2$ values from $–31.44$ to -24.65 at 250 and 400°C, respectively. In the case, Mgt is stable in runs along with others of pyrite-hematite-magnetite (PHM) mix. Estimated "in situ" pH values, generated by the associations (1, 2) are shown in figure 1 together with those of starting solutions and PHM buffer.
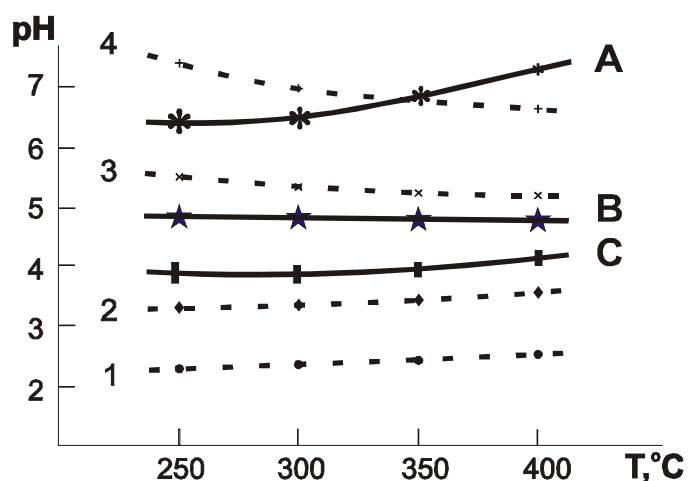

Fig. 1. T-pH diagram of "in situ" values calculated for the mineral associations and starting chloride solutions
    A – the sulfur free association (1);
    B – the association (2);
    C – the position of PHM buffer; dashed lines denote start solutions without the solids charge: 1mNaCl + 10^{-2}mHCl (1), 1mNaCl+10^{-3}mHCl (2), 1mNaCl (3), 1mNaCl+10^{-3}mNaOH (4).

The low total gold solubility calculated for the sulfur free medium is related to a lack of information on hydroxocomplexes of gold in SUPCRT98 data file. Control estimation in a few points by the "Gibbs" package using the UNITERM data set [3], including the Au-hydroxocomplexes, yields calculated results that are closely related to measured values. The dominant role of hydrosulfide species ascertained by calculation explains the increase in total dissolved Au content with introduction of sulfur into the system. Nevertheless, it must be noted that the current thermodynamic explanation of gold speciation, especially in complex solutions, is far from reality. In this regard, the interactions between gold forming ligands should be taken properly into account [6].

Thus, very low solubility of total gold was measured for the sulfur less propylites, which present an effective geochemical burrier for gold deposition (on the threshold concentration is 0.004mg/L at 300°C/1 kb). The advent of sulfur in the system increases the last up to 0.075 mg/L and favors gold acquisition in a fluid.

References:

[1] *Plyusnina L.P.* 1990. Experimental study of stability of epidote in chloride-carbonate solutions. Geokhimiya. No1. P. 26-35 (in Russian).

[2] *Chudnenko K.V., Karpov I.K., Bychinski V.A., and Kulik D.A.* 1995. Current status of the SELEKTOR software package. In Y. KHARAKA & O. CHUDAEV (Eds.) Water-Rock Interaction A.A. Balkema P. 725-727.

[3] *Shvarov Yu.V.* 1999. Algorithmization of the numeric equilibrium modeling of dynamic geochemical processes. Geochem. Intern. V.37. P. 571-577.

[4] *Hayashi K., and Ohmoto H.* 1991. Solubility of gold in NaCl and H_2S-bearing aqueous solutions at 250-350°C. Geochim. Cosmochim. Acta V.55. P. 2111-2126.

[5] *Johnson J.W., Oelkers E.H., and Helgeson H.C.* 1992. SUPCRT 92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0° to 1000°C. Computer and Geosciences. V.77. P. 899-947.

[6] *Likhoidov G.G., Nekrasov I.Ya*. 2001. Gold solubility in complex sulfide-chloride fluids at 300-500°C and P_{tot} = 1 kb. Geochem. Intern. V.39. P. 347-355.