

Thermodynamic evaluation of silver reprecipitation in the zones of supergene oxidation

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The role of sulphide minerals in the process of Ag reprecipitation during the supergene alteration of polymetallic ores has been evaluated using the databases WATEQ4F (Ball and Nordstrom, 1991) and SUPCRT'92 (Johnson *et al.*, 1992). Four common principle oxidation stage were fixed previously with formation of the following Ag-products, when oxygen fugacity decreases:

(1) cerargyrite $\text{AgCl}_{(s)}$ below the residual ore zone at $\lg f_{\text{O}_2, \text{atm}} < -30$, when $(\text{Ag}^+)(\text{Cl}^-) > 10^{-9.75} \text{ mol/l}$;

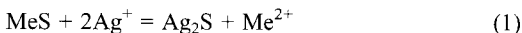
(2) $\text{Ag}_{(s)}$ in the upper part of the zone of oxidation. Corresponding to the differences in Eh-pH regimes, the Ag^+ activity can vary within the limits:

$\lg f_{\text{O}_2, \text{atm}}$	pH	$\lg a_{\text{Ag}^+, \text{mol/l}}$
-30 -40	3	-3.23 -5.73
-40 -50	4	-6.73 -9.23;

(3) Ag_2S in the zone of secondary ore enrichment at $\lg f_{\text{O}_2, \text{atm}} > -60.6$, when $\text{pH} = 3$, $a_{\text{SO}_4^{2-}} = 10^{-3} \text{ mol/l}$;

(4) $\text{Ag}_{(s)}$ in reducing environment as the ground-water percolates to greater depth.

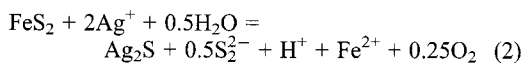
$\text{Ag}_{(s)}$ reprecipitation in the upper part of the zone of oxidation needs relatively high Ag^+ activity in acid solutions and can proceed only at near-neutral pH or at $f_{\text{O}_2, \text{atm}}$ much lower than 10^{-40} . But the interaction of silver ion with residual pyrite, galena and sphalerite takes place. The cation-exchange reactions have negative Gibbs free energy, and thus could proceed spontaneously under ambient conditions:



here Me are Pb ($\Delta G_{\text{reaction}} = -31.74 \text{ kcal/mol}$) and Zn (-33.33 kcal/mol).

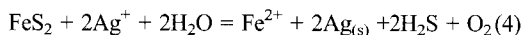
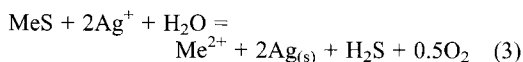
Recent spectroscopic investigation of sulphide minerals surface after their interaction with Ag^+ -containing solutions confirmed the formation of Ag_2S as the first product (Scaini *et al.*, 1995). It is in accordance with last Sato's diagrams (Sato, 1992). If the Me^{2+} activities are 10^{-6} mol/l , the needed Ag^+ to precipitate on the surface of PbS are $10^{-14.6} \text{ mol/l}$ and ZnS - $10^{-15.2} \text{ mol/l}$. The use of field chemical analyses can correct these values because the excess of metals shifts the equilibrium left. The behaviour of pyrite is more flexible and depends on

numerous variables:



For the accepted Me^{2+} activity equal to S_2^{2-} and $\text{pH} = 3$, the needed Ag^+ to precipitate on the surface of FeS_2 is $10^{-15.08} \text{ mol/l}$.

The next reactions can be attributed to reduced redox potentials:



Hereafter the activities of Ag^+ at $\text{Me}^{2+} = 10^{-6} \text{ mol/l}$ and $\lg f_{\text{O}_2, \text{atm}} = -70$ are shown:

Sulphide mineral	$\lg a_{\text{Ag}^+, \text{mol/l}}$
PbS	-13.34
ZnS	-13.92
FeS_2	-14.82

The results of our preliminary study indicate that the reprecipitation of silver on sulphide minerals could take place at very low activity of Ag^+ ; and at the equal activities of Me^{2+} the following order of potential precipitants is: FeS_2 - ZnS - PbS.

The computer thermodynamic model following this simplified general scheme, with the use of free energy minimizing codes and some natural (field) chemical analyses is in elaboration now and will be presented during Conference.

References

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