Hydrosulphide complexes of gold (I) at high pressures and temperatures: equilibrium and kinetic problems

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Introduction

In most solubility experiments at high pressures and temperatures the achievement of equilibrium and the understanding of the reaction kinetics are of major importance. In this paper we discuss problems that occurred during our experiments on gold(I) complexing in hydrosulphide solutions. The experiments were carried out in order to confirm the stability of the $AuHS^0$ complex in near-neutral to acid pH solutions from 150 to 500°C, at 500 bar. The results could have important implications on the approach to equilibrium in studies of this type.

Experimental methods

The experiments were conducted in rocking autoclaves with flexible gold reaction-cell systems such that the solutions were only in contact with gold. The oxidation potential was maintained by introducing a constant partial pressure of hydrogen gas inside the cell as well as in the pressure medium (water) surrounding the gold cell (Benning and Seward, 1993). In order to control the effect of the disproportionation of H_2S, some experiments at acid pH conditions were conducted without controlling the oxidation potential (i.e. no added H_2 gas). Samples for gold and hydrogen analysis were extracted while the autoclave was held at constant high temperature and pressure. Gold concentrations were measured by ICP-MS and H_{2tot} by GC. Equilibrium solubilities were attained within 1–3 days or less at all temperatures. Reversed data were obtained only at $T >$ 300°C. At temperatures below 300°C, when equilibrium is approached from supersaturation, the solubility initially decreases to as much as 50% below the equilibrium value obtained by approach from undersaturation. With time, the solubilities then slowly increase and begin to converge (over a period of weeks) towards the equilibrium value approached previously from undersaturation. The reason for this over-shooting of the equilibrium solubility when approached from supersaturation

is not clear. However, a possible explanation may lie in the formation of gold colloids which then scavenge gold from solution. Further work is underway to try to clarify this problem.

Hydrosulphide complexes

It is generally accepted that, for the system in question in the near-neutral pH region, the dominant complex is $Au(HS)_2^-$. Two complexes have been proposed to predominate in the acid pH region: $AuHS^0$ (Seward, 1973; Renders and Seward, 1989) and $HAu(HS)_2^0$ (Hayashi and Ohmoto, 1991). The data presented in this paper spread over a wide enough range of total sulphur concentrations to confirm that the species $AuHS^0$ is the stable complex at temperatures up to 300°C. Plotting log $m_{Au,tot}$ vs. log $m_{S,tot}$ an ideal slope of 0.5 for the species $AuHS^\circ$ is expected while a slope of 1.5 would indicate the species $HAu(HS)_2^0$. For example, the best fit line for the experimental points at 250°C has a slope of 0.64, which confirms that the complex $AuHS^0$ is the dominant species under these conditions (Fig. 1).

The complex formation of the species $AuHS^0$ can be represented by the dissolution reaction:

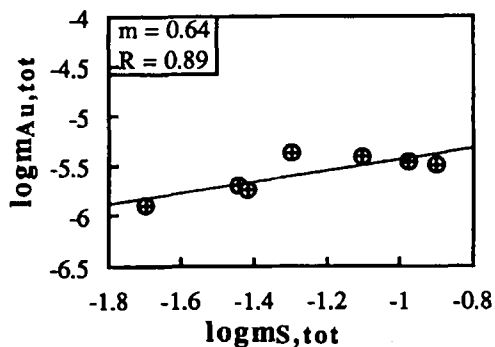Fig. 1. Plot of log m $_{Au,tot}$ vs. log $m_{S,tot}$ at 250°C and $pH_{(250°C)} \approx 4.0$. The slope of the best fit line is close to the ideal slope of 0.5 for the species $AuHS^0$.

$$Au_{(s)} + H_2S(aq) \rightleftharpoons AuHS^0 + \tfrac{1}{2}H_{2(gas)} \qquad (1)$$

The calculated preliminary log K values for the species $AuHS^0$ are given in Table 1. It should be noted that there is a computational error in the log K values reported earlier by Benning and Seward (1993).
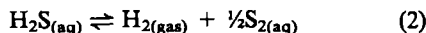
TABLE 1. Log K data for the species $AuHS^{\circ}$ at 500 bar

t (°C)	log K
25*	−11.14 ± 0.20
150	−5.46 ± 0.41
200	−5.42 ± 0.20
250	−5.43 ± 0.22
300	−5.91 ± 0.20

* the 25°C value is from Renders and Seward (1989).

Fig. 2. Plot of the $m_{H2,disp.}$ produced by the disproportionation reaction (2) corrected for H_2 produced by reaction (1) and the $m_{Au,tot}$ vs. time in hours at 200°C at 500 bar in a solution with $m_{S,tot} = 0.0625$.

H_2S disproportionation and implications

A number of experiments were performed in order to study the kinetics of H_2S disproportionation in aqueous media at elevated temperatures and pressures. H_2S solutions were maintained at constant T and P (no added hydrogen!) and both the hydrogen and gold concentrations monitored as the H_2S disproportionation (reaction 2) proceeded. Even after 30 days at 200°C, the redox equilibrium had not been established (Fig. 2) and the progressive disproportionation of H_2S was still continuing after 1.5 months. These observations emphasize the problem in trying to control or maintain a known hydrogen fugacity in hydrothermal experiments by assuming attainment of equilibrium amongst aqueous sulphur species as described by reaction 2 and 3:

$$H_2S_{(aq)} \rightleftharpoons H_{2(gas)} + \tfrac{1}{2}S_{2(aq)} \qquad (2)$$

$$H_2S_{(aq)} + 2H_2O_{(l)} \rightleftharpoons HSO_4^- + H^+ + 2H_{2(g)} \qquad (3)$$

Shenberger and Barnes (1989) have commented on the difficulty in attaining equilibrium gold solubilities at t < 300°C in their experiments involving reduced/oxidised sulphur redox equilibria. In the present experiments, we have avoided this problem by working wi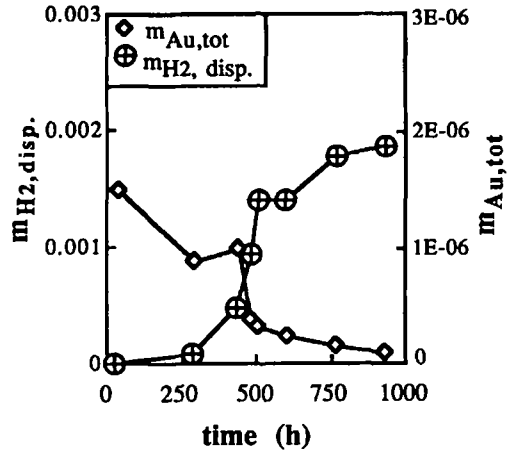th known, fixed hydrogen partial pressures much in excess of those associated with the equilibrium disproportionation of H_2S.

Conclusions

High temperature hydrothermal fluids in the crust carry significant concentrations of gold in form of hydrosulphide complexes. The maximum solubility coincides with pH = pK_1 (H_2S) which at higher temperatures shifts progressively to higher values (e.g. $pK_1 \approx 9.0$ at 350°C). The pH of maximum stability for the species $Au(HS)_2^-$ therefore shifts to more alkaline values and the complex $AuHS^{\circ}$ becomes the dominant species in lower pH, rock-buffered high temperature fluids.

References

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