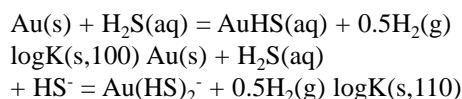# Gold(I) Complexing by Sulphide Ligands in Hydrothermal Solutions to 450 ºC at 500 bar

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A knowledge of the stability of aqueous gold(I) complexes in hydrothermal solutions is essential for quantitative interpretation of the transport and deposition mechanisms of gold by hydrothermal fluids in the crust. It is generally excepted that in dilute, reduced, natural geothermal waters, gold is transported predominantly as Au(I) hydrosulphide/sulphide complexes. However, some inconsistencies exist between the experimentally derived stoichiometry and stability of Au(I) hydrosulphide complexes, especially at high temperatures and pressures. The solubility of pure gold (99.99%) was measured in dilute sulphide solutions up to 450 ºC and 500 bar. The experiments were carried out in a flow-through autoclave, connected to an HPLC pump and back-pressure regulator on line. This approach provided several advantages over static experiments for solubility measurements. All components could be measured without disturbing the chemical equilibrium, experimental time was in the orders of few minutes minimizing the problem of loss of volatile components like hydrogen and hydrogen sulphide and many replicate samples could be taken. Solutions for the experimental runs were prepared from triple-distilled water that had been deoxygenated by boiling under vacuum and by bubbling oxygen free argon gas through the solutions. The pH of the solutions was adjusted by addition of NaOH (0-0.018 m) or HCl (0-0.030 m). Reduced sulphur and hydrogen were added to the solutions by bubbling a known $Ar+H_2S+H_2$ gas mixture through the solution for 15-20 minutes. For every experimental run at a given temperature and pressure, several samples were taken and analysed for total reduced sulphur, dissolved gold (AA and ICP-MS) and for hydrogen (GC). Total dissolved Au measured in the solutions was in the range 3.1×10^{-8} to 1.7×10^{-4} m, total reduced sulphur between 1.6×10^{-2} and 13×10^{-2} m, total dissolved hydrogen between 0.016×10^{-4} and 1.3×10^{-3} m, and the pH_Tp varied from 1.5 to 9.8 under experimental conditions. A non-linear least squares treatment of the data demonstrate that the solubility of gold in hydrosulphide solutions up to pH 7 (at 25 ºC), can be accurately described by the reactions

$$Au(s) + H_2S(aq) = AuHS(aq) + 0.5H_2(g)$$
$$logK(s,100) \quad Au(s) + H_2S(aq)$$
$$+ HS^- = Au(HS)_2^- + 0.5H_2(g) \quad logK(s,110)$$

where AuHS(aq) is the dominant species under acidic conditions and $Au(HS)_2^-$ under mildly acidic to neutral pH conditions. The equilibrium constants calculated from the solubility data are in the range of $-logK(s,100) = +7.9 - +6.7$ and $-logK(s,110) = +1.7 - +1.0$ at 100-440 ºC and 500 bar. The uncertainties on these equilibrium constants are on the order of 0.05 logK. In the present study a self-consistent thermodynamic data set on the stability for Au(I) hydrosulphide complexes was produced with the accuracy of the data depending only on the uncertainties of the measured solute concentrations and the H_2S ionisation constants measured in our laboratory.