Appendix

Thermodynamic properties of Au aqueous species and equilibrium calculations of Au solubility and speciation

Speciation calculations were performed using the GIBBS computer code implemented in the HCh software package (Shvarov, 1999; Shvarov and Bastrakov, 1999). The activity coefficients of aqueous species were calculated according to Helgeson (1969). The ion size parameter å was taken to be equal to 4.5 Å for all species. The thermodynamic properties of water and most aqueous species (except those for Au-Cl and Au-OH complexes) were adopted from the SUPCRT92 database (Johnson et al., 1992), and those of $NaSO_4^-$ were taken from Pokrovski et al. (1995). The data sources for Au-Cl and Au-OH aqueous complexes are discussed in detail below.

$Au(OH)_2^-$, $AuCl^0_{(aq)}$, and $AuCl_2^-$

The thermodynamic properties of $Au(OH)_2^-$, $AuCl^0_{(aq)}$, and $AuCl_2^-$ were computed using HKF model parameters reported in Akinfiev and Zotov (2001). In that study, thermodynamic properties of $AuCl_2^-$, which dominates gold aqueous speciation at high temperatures in our EXAFS experiments, were obtained by regression of the experimental data of Zotov and Baranova (1989) (gold solubility measurements, 350-500°C, 500-1500 bars), Gammons and Williams-Jones (1995) ($AgCl_{(s)}$ + Ag-Au alloy solubility measurements, 300°C, P_{sat}), and Nikolaeva et al. (1972) (potentiometric determination of the equilibrium constant for the reaction $AuCl_2^- + e^- = Au_{(s)} + 2\ Cl^-$, 25-80°C and P_{sat}). The experimental data of Zotov and Baranova (1989) are in excellent agreement with recent experimental gold solubility determinations by Stefánsson and Seward (2003b) (see Table 9 in Stefánsson and Seward, 2003b). For consistency, we use the thermodynamic properties of $AuCl_2^-$ from Akinfiev and Zotov (2001) since they cover the complete *T-P* range of our experiments and are based on thermodynamic data for H_2O, and aqueous HCl, NaCl and H_2 which are employed in the present study.

936 *$AuCl_4^-$*

937 The only thermodynamic dataset for $AuCl_4^-$ that enables calculation of its' thermodynamic properties
938 at the *T-P* conditions of the present study is that of Sverjensky et al. (1997). However, this dataset is based
939 entirely on the HKF-model correlations and is inconsistent with the available experimental data as well as
940 with the Au^{III}/Au^{I} ratios determined in the present study. Therefore, we performed our own compilation of
941 the literature experimental data for $AuCl_4^-$. There are two studies available in the literature which report
942 measurements of equilibrium constants of reactions between $AuCl_4^-$ and $AuCl_2^-$. Nikolaeva et al. (1972)
943 potentiometrically determined the standard potential at 25-150°C at an ionic strength of 1.0 for the reaction

944 $$AuCl_4^- + 2e^- = AuCl_2^- + 2\,Cl^- \quad (1)$$

945 Gammons et al. (1997) determined Au^{I} and Au^{III} concentrations in equilibrium with metallic gold at 100-
946 200°C and reported the equilibrium constant for the reaction

947 $$3AuCl_2^- = 2Au_{(s)} + AuCl_4^- + 2Cl^- \quad (2)$$

948 The equibrium constants of reactions 1 and 2 were extrapolated to the standard state conditions using the
949 extended Debye-Hückel model (Helgeson, 1969) and fitted to the modified Ryzhenko-Bryzgalin electrostatic
950 model (Ryzhenko, 1981, Bryzgalin and Rafal'skiy, 1982, Plyasunov and Grenthe, 1994). This is a simple
951 electrostatic model which describes the Gibbs free energy of a reaction $\Delta_r G^o(T,P)$ as a sum of
952 nonelectrostatic and electrostatic contributions

953 $$\Delta_r G^o(T,P) = \Delta_r G^o_{nonel} + \Delta_r G^o_{electr}(T,P) \quad (3)$$

954 The nonelectrostatic term is assumed to be independent of temperature and pressure, whereas the *T-P*
955 dependent electrostatic term accounts for the changes of the dielectric permittivity of water with *T* and *P*.
956 The regression of the experimental values between 25-200°C for the $AuCl_4^-$ dissociation constant (K_{dis})

957 $$AuCl_4^- = Au^+ + 4\,Cl^- \quad (4)$$

958 was performed with the aid of the UT-RYZ program which is a part of the HCh package and using the
959 thermodynamic properties of Au^+ from the SUPCRT92 database. The program fits the experimental values
960 of the dissociation constants to the equation

961 $$-\log K_{dis} = pK_{dis} = \frac{T_r}{T} \cdot pK_{dis}(T_r, P_r) + C(T,P) \cdot \frac{\left|Z_i Z_j\right|_{eff}}{a_{eff}} \quad (5)$$

with $\frac{|Z_i Z_j|_{eff}}{a_{eff}} = A + \frac{B}{T}$, where pK_{dis}, A and B are the regression parameters, and T_r and P_r stand for the reference temperature and pressure, respectively (298.15 K and 1 bar). The parameter $C(T,P)$ is independent of the nature of the species and was computed from the T-P dependence of the dissociation constant of pure water (Marshall and Frank, 1981) and assuming that $\frac{|Z_i Z_j|_{eff}}{a_{eff}}$ = 1.0107. More details of the Ryzhenko-Bryzgalin model are given in Plyasunov and Grenthe (1994).

The values pK_{dis} (25°C, 1 bar) = 26.15 ± 0.14, A = 3.352 ± 0.09, and B = 0 (fixed during regression) were computed for the $AuCl_4^-$ dissociation reaction (4). The pK_{dis} values generated using these parameters and Eqn. (5) match the experimental data of Nikolaeva et al. (1972) to 100°C and Gammons et al. (1997) to 200°C within better than 0.1 pK, whereas the agreement with the Nikolaeva et al. (1972) data is within ~0.15 and ~0.40 pK at 125 and 150°C, respectively, which is comparable with their experimental uncertainties (± 0.1 and ±0.3 pK at 125 and 150°C, respectively). Note, however, that in low-density fluids (< 0.4 g/cm^3) at temperatures above 400°C, the electrostatic model predictions become unreliable and large uncertainties are expected for pK_{dis} (> 1 pK) calculated for XAFS experiments 5 and 6 of this study.

$AuOH^0_{(aq)}$

The only thermodynamic dataset for $AuOH^0_{(aq)}$ was published by Akinfiev and Zotov (2001). However, their compilation was entirely based on the experimental gold solubility data of Zotov et al. (1985) between 300 and 500°C at 500-1500 bar and did not consider the experimental study of Au solubility in H_2O-NaOH solutions performed at 25°C by Vlassopoulos and Wood (1990), which reports the only available data for $AuOH^0$ at 25°C/1 bar. The restricted T-range of the Zotov et al. (1985) data prohibits accurate extrapolation of $AuOH^0$ stability constants to ambient conditions, resulting in anomalously high concentrations of $AuOH^0$ at temperatures below 300°C as predicted by Akinfiev and Zotov (2001). Stefánsson and Seward (2003) report stability constants for $Au(OH)^0_{(aq)}$ based on their Au solubility determinations at 300-600°C and 500-1500 bar. The $AuOH^0$ formation constants reported in that study are in close agreement (within 0.4 log units) with the data of Zotov et al. (1985). Because the van't Hoff equation

coefficients for the $AuOH^0$ formation constant reported in Stefánsson and Seward (2003a) do not allow their interpolation with respect to pressure we, therefore, calculated, with the aid of the Ryzhenko-Bryzgalin electrostatic model, two independent sets of equilibrium constants for the reaction

$$AuOH^0_{(aq)} = Au^+ + OH^- \quad (6)$$

i) a first set was obtained by regression of the experimental data of Zotov et al. (1985) and Vlassopoulos and Wood (1990), pK_{dis} (25°C, 1 bar) = 20.00 ± 1.56, A = 0.677 ± 0.175, and B = 0; and ii) a second set was generated by regression of the experimental data of Stefánsson and Seward (2003a) and Vlassopoulos and Wood (1990), pK_{dis} (25°C, 1 bar) = 19.85 ± 0.70, A = -0.777 ± 0.300, and B = 1047 ± 239.

Results of speciation calculations performed with these thermodynamic datasets for $AuCl_4^-$ and $AuOH^0_{(aq)}$ are given in the Supplementary Table and compared with the experimental results of the present study in Section 4.2. Supplementary Table shows Au speciation in the experimental solutions calculated using the two sets of thermodynamic data for $AuOH^0_{(aq)}$ and the thermodynamic properties for Au-Cl species discussed above. The set based on the $AuOH^0$ formation constants from Zotov et al. (1985) yields stabilities of $AuOH^0$ at $T \leq 300$°C which are in good agreement with the Au speciation determined from XAFS measurements in present study.

1003 **Supplementary Table**

1004 Calculated dissolved gold concentrations (in mol/kg of H_2O) and fraction of dominant Au
1005 species in the investigated systems at 600 bar as a function of temperature.
1006

T °C	mAu	$AuCl_4^-$ %	$AuCl_2^-$ %	$AuCl^0$ %	$AuOH^0$ %
Stability of $AuOH^o$ is determined via regression of experimental data from Zotov et al. (1985) and Vlassoupoulous and Wood, 1990					
$Au_{(s)}$-0.032m $HAuCl_4$-0.53m NaCl-0.53m HCl					
22	0.032	97.7	2.2	< 1	< 1
250	0.091	2.6	88.2	8.9	< 1
0.035m $HAuCl_4$-0.50m NaCl-0.01m HCl					
30	0.035	100	< 1	< 1	< 1
100	0.035	99.9	< 1	< 1	< 1
150	0.035	99.5	< 1	< 1	< 1
200	0.035	97.9	1.5	< 1	< 1
250	0.035	93.8	4.9	1.0	< 1
300	0.035	85.4	12.5	1.6	< 1
$Au_{(s)}$-0.035m $HAuCl_4$-0.50m NaCl-0.01m HCl					
30	0.035	98.0	1.7	< 1	< 1
100	0.039	84.1	11.2	1.9	2.9
150	0.048	58.3	28.7	6.4	6.6
200	0.069	26.5	53.3	12.1	8.1
250	0.094	6.1	73.2	14.2	6.6
300	0.10	< 1	82.9	12.1	4.3
400	0.10	< 1	93.9	7.5	2.0
$Au_{(s)}$-2.6m NaCl – 0.53m H_2SO_4					
300	$5.1 \cdot 10^{-4}$	< 1	96.0	4.0	< 1
400	$7.2 \cdot 10^{-3}$	< 1	97.4	2.5	< 1
*500 **	*0.014*	*40.2*	*58.0*	*1.0*	*< 1*
Stability of $AuOH^o$ is determined via regression of the experimental data from Stefánsson and Seward, 2003 and Vlassoupoulous and Wood, 1990					
$Au_{(s)}$-0.032m $HAuCl_4$-0.53m NaCl-0.53m HCl					
22	0.032	97.7	2.2	< 1	< 1
250	0.091	2.5	86.2	8.7	2.6
0.035m $HAuCl_4$-0.50m NaCl-0.01m HCl					
30	0.035	100	< 1	< 1	< 1
100	0.035	99.9	< 1	< 1	< 1
150	0.035	98.8	< 1	< 1	1.0
200	0.035	96.3	1.5	< 1	2.5
250	0.035	92.1	3.9	< 1	3.3
300	0.035	84.6	11.5	1.5	2.4
$Au_{(s)}$-0.035m $HAuCl_4$-0.50m NaCl-0.01m HCl					
30	0.035	98.0	1.7	< 1	< 1
100	0.043	71.4	10.0	1.6	17.0
150	0.064	32.3	20.4	4.3	43.1
200	0.086	11.0	36.3	7.5	45.3
250	0.10	2.6	55.7	9.9	31.9
300	0.10	< 1	73.1	10.2	16.2
400	0.10	< 1	90.5	7.5	1.6
$Au_{(s)}$-2.6m NaCl – 0.53m H_2SO_4					
300	$5.1 \cdot 10^{-4}$	< 1	95.6	3.9	< 1
400	$7.2 \cdot 10^{-3}$	< 1	97.4	2.5	< 1
*500°C, 600 bar**	*0.014*	*40.2*	*58.0*	*1.0*	*< 1*
500, 800 bar	0.026	< 1	98.0	1.7	< 1

1007 * calculations for 500°C, 600 bar are highly uncertain due to restrictions of both HKF and Ryzhenko
1008 models at densities below 0.4 g/cm^3.

References for Appendix

Akinfiev, N.N., Zotov, A.V., 2001. Thermodynamic description of chloride, hydrosulphide, and hydroxo complexes of Ag(I), Cu(I), and Au(I) at temperatures of 25-500°C and pressures of 1-2000 bar. Geochem. Intern. 39 (10), 990-1006.

Bryzgalin, O.V., Rafal'skiy, R.P., 1982. Estimation of instability constants for ore-element complexes at elevated temperatures. Geochem. Intern. 19, 839-849.

Gammons, C.H., Williams-Jones, A.E, 1995. The solubility of Au-Ag alloy + AgCl in HCl/NaCl solutions at 300°C: new data on the stability of Au(I) chloride complexes in hydrothermal fluids. Geochim. Cosmochim. Acta 59, 3453-3468.

Gammons, C. H., Williams-Jones, A.E., 1997. The disproportionation of gold(I) chloride complexes at 25 to 200°C. Geochim. Cosmochim. Acta 61, 1971-1983.

Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. Amer. J. Sci. 267, 729-804.

Johnson, J.W., Oelkers, E.H., Helgeson, H.C., 1992. SUPCRT92: 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. Comput. Geosci. 18, 899-947.

Marshall, W.L., Franck, E.U. (1981) Ion product of water substance, 0-1000°C, 1-10000 bars. New international formulation and its background. J.Phys. Chem. Ref. Data 10, 295-304.

Nikolaeva, N.M., Erenburg, A.M., Antipina, V.A., 1972. About the temperature dependence of the standard potentials of halogenide complexes of gold. Izvestiya Sibirskogo Otdeleniya AN SSSR, No. 9, Ser. Khim. Nayk, Vip. 4, 126-128 (in Russian).

Plyasunov, A.V., Grenthe, I., 1994. The temperature dependence of stability constants for the formation of polynuclear cationic complexes. Geochim. Cosmochim. Acta 58, 3561-3582.

Pokrovski, G.S., Schott, J., Sergeyev, A.S., 1995. Experimental determination of the stability constants of $NaSO_4^-$ and $NaB(OH)_4^0$ in hydrothermal solutions using a new high-temperature sodium-selective glass electrode: Implications for boron isotopic fractionation. Chem. Geol. 124, 253-265.

Ryzhenko, B.N., 1981. Equilibria in Hydrothermal Solutions. Nauka, Moscow (in Russian).

Shvarov, Yu.V, Bastrakov, E.N., 1999. HCh: a software package for geochemical equilibrium modelling. User's Guide. Australian Geological Survey Organization, Record 1999/25.

Shvarov, Yu.V., 1999. Algorithmization of the numeric equilibrium modelling of dynamic geochemical processes. Geochem. Intern. 37, 571-576.

Stefánsson, A., Seward, T.M., 2003a. The hydrolysis of gold(I) in aqueous solutions to 600°C and 1500 bar. Geochim. Cosmochim. Acta 67, 1677-1688.

Stefánsson, A., Seward, T.M., 2003b. Stability of chloridogold(I) complexes in aqueous solutions from 300 to 600°C and from 500 to 1800 bar. Geochim. Cosmochim. Acta 67, 4559-4576.

Sverjensky, D.A., Shock, E.L., Helgeson, H.C., 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb. Geochim. Cosmochim. Acta 61, 1359-1412.

Vlassopoulos, D., Wood, S. A., 1990. Gold speciation in natural waters: I. Solubility and hydrolysis reactions of gold in aqueous solution Geochim. Cosmochim. Acta 54, 3-12.

Zotov, A.V., Baranova, N.N., 1989. Thermodynamic properties of the aurochloride solute complex $AuCl_2^-$ at temperatures of 350-500°C and pressures of 500-1500 bars. Sci. Géol. Bull. 42, 335-342.

Zotov, A.V., Baranova, N.N., Dar'yna, T.G., Bannykh, L.N., Kolotov, V.P., 1985. The stability of $AuOH^0_{sol}$ in water at 300-500°C and 500-1500 atm. Geochem. Intern. 22 (5), 156-161.