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Experimental investigation of Pd solubility and speciation in H_2O-HCl liquids: Implications for the formation of hydrothermal palladium deposits.

Par

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SUMMARY

Although existing models for the formation of PGE deposits have been built on the assumption that metal concentration is effected by magmatic processes, there is strong evidence that hydrothermal processes may involving chloride-bearing aqueous liquids also play an important role in concentrating these metals (particularly palladium). In view of this we have investigated the solubility and speciation of palladium experimentally in HCl-H_2O liquids at elevated temperatures. The formation constants of Pd complexes in chloride solutions have been determined spectrophotometrically at temperatures of 25 to 250 °C and a pressure of 50 bar. $PdCl_4^{2-}$ is the dominant species over the range of temperatures investigated. However, $PdCl_3^-$ is important at temperatures above 200°C. Cumulative formation constants calculated for the species $PdCl_4^{2-}$, $PdCl_3^-$, $PdCl_2^o$and $PdCl^+$ are provided by the following equations:

$$Pd^{2+} + Cl^- \quad = \quad PdCl^+ \ \beta_{1,0};$$

$$Pd^{2+} + 2\cdot Cl^- \quad = \quad PdCl_2^o \ \beta_{2,0};$$

$$Pd^{2+} + 3\cdot Cl^- \quad = \quad PdCl_3^- \ \beta_{3,0};$$

$$Pd^{2+} + 4\cdot Cl^- \quad = \quad PdCl_4^{2-} \ \beta_{4,0};$$

Values of log □ calculated for these equations are close to those extrapolated from low temperature data by Wood et al. (1992) and determined experimentally by Gammons (1993) but diverge sharply from those predicted using the correlation methods of Sassani and Shock (1998). The data obtained suggest that the species $PdCl_4^{2-}$, $PdCl_3^-$ are more stable at elevated temperatures than was previously thought. Extrapolation of the data to temperatures above 300° C, suggests that the solubility of Pd at slightly acidic pH and intermediate fO_2 is high enough to concentrate this metal to potentially economic levels in natural hydrothermal systems.

1. INTRODUCTION

1.1 Objectives

Recent advances in catalytic converter and fuel cell technology have led to a sharp increase in demand for palladium, and a corresponding increase in the exploration for this metal, particularly in North America where production has been relatively limited. Although, it is well-established that the most important PGE deposits occur in mafic-ultramafic intrusions and that initial metal concentration is dominated by magmatic processes (cf. Barnes and Maier, 2002), there is strong evidence that hydrothermal processes may play an important role in remobilizing these metals (particularly Pd) and locally increasing their concentrations to economic levels (e.g, Li and Naldrett, 1993; Farrow et al., 1994; Ripley and Chryssoulis, 1994). There is also evidence that Pd may be concentrated exclusively by hydrothermal processes in other environments (e.g., Yang et al., 1974; Faramazyan et al., 1975; Werle et al., 1984; McKibben et al., 1990; Helmy et al., 1995).

Québec hosts several ore deposits that contain significant concentrations of PGE's, although in none of these is Pd a major commodity. However, the geology of Québec is characterized numerous mafic-ultramafic intrusive bodies, and there is thus considerable potential for the discovery of new Pd-bearing deposits (Clark, 2001). Despite this, our understanding of how Pd is concentrated and particularly the role of hydrothermal processes in this concentration is extremely is extremely limited. Consequently we are very ill-equipped to predict where this metal is likely to be enriched and to develop tools for its exploration.

The objective of our study was to contribute to our understanding of the hydrothermal controls on Pd concentration by conducting experiments designed to investigate the speciation and solubility of Pd in aqueous fluids. This report summarizes the results of a study of the behaviour of Pd in chloride-bearing aqueous fluids, which we believe provide reasonable analogs for the types of fluids that are likely to concentrate palladium in nature.

1.2 Background and state of knowledge

Palladium dissolution in chloride-bearing aqueous liquids is a complex phenomenon involving formation of at least four simple chloride species (from PdCl to $PdCl_4$; e.g., Sassani and Shock, 1998), several hydroxide and hydroxychloride species (e.g., Middlesworth and Wood, 1999; Byrne and Yao, 2000; Cosden and Byrne, 2003) and an unknown number of polymerised species (e.g., Pd3Cl6; Gammons, 1995). Despite their potential importance in controlling the transport of palladium in nature, the chemical behaviour of these species is poorly known and there have been very few experimental studies of the solubility of Pd, especially at elevated temperatures. Orlova et al. (1987) and Hsu et al. (1991) investigated the solubility of Pd metal in aqueous chloride solutions from 300 to 700°C, but their data are very difficult to interpret because of a lack of information on pH and fO_2 during the experiments. Although the data from the studies below 300 °C (e.g., Gammons, 1995) can be interpreted reliably, they were mostly obtained using indirect solubility methods and cannot be extrapolated to higher temperatures due to the complexity of Pd speciation. The solubility method used in the above studies is well-suited to determining the stability of species in systems where there is a small number of dominant species involving a single ligand. However, interpretation of data obtained using this method for more complex systems, involving larger number of species and multiple ligands, can be difficult and can lead to equivocal solutions. By contrast, the ultraviolet-visible spectrophotometric method provides an *in situ* record of the electronic spectra of complexes present in detectable concentrations, thereby allowing their identification. In many cases, these spectra can be used to determine the corresponding concentrations of these species and in turn their stability constants. Previous spectrophotometric studies designed to investigate the speciation of Pd in chloride-bearing aqueous solutions have been restricted to temperatures <90 °C (Tait et al., 1991; Byrne and Yao, 2000; Cosden and Byrne, 2003) and consequently Pd speciation in chloride-bearing aqueous liquids remains poorly understood at elevated temperatures.

2. METHOD

In order to obtain data on Pd speciation in Cl-bearing solutions, we have designed a spectrophotometric system (Figure 1), which permits direct identification and measurement of concentrations of all species absorbing radiation in the UV-visible region of the electromagnetic spectrum. The first set of experiments was performed using a high temperature spectrophotometric cell, equipped with sapphire windows, which allows *in situ* recording of solution spectra at elevated temperatures and pressures. The cell, which is constructed of titanium (Grade IV), was heated using heating elements introduced into the cell body. Temperature was controlled by an Omega CN-2001 regulator with a type K thermocouple inserted in a thermocouple well drilled into the cell. This permitted the temperature of the experiment to be maintained to within an error of ± 0.5 °C. Pressure was controlled using a solution delivery system, consisting of HP 1050-Ti HPLC pump, PEEK and Ti capillaries, and a PEEK back pressure regulator. Experimental solutions were therefore only in contact with chemically inert materials. The system was operated at flow rates of 0.1 to 0.3 ml/min, providing complete exchange of the solutions in the cell in 10 to 3 minutes, respectively. At temperatures above 250 °C, interpretation of UV-vis spectra is difficult, especially if hydroxyl and hydroxychloride complexes are present, and typically requires that run temperature pH be accurately estimated. In order to accomplish this second stage of the study, we have developed a high temperature potentiometric system, which we have coupled on-line to the spectrophotometric cell. This new system permits *in situ* pH control at temperatures up to 450 °C. The second stage experiments are currently in progress, and will be completed by the end of August.

Spectrophotometric measurements were made at 0.2 nm intervals over the range 190 to 400 nm. The path length (0.98 cm) was determined by a calibration procedure involving measurements of the absorption of a $3\cdot10^{-3}$ mol/dm3 potassium iodide solution at 25 °C in a standard 1 cm quartz cuvette and in the flow-through cell. Absorption spectra were collected for 19 solutions with total Pd concentrations ranging from $1.15\cdot10^{-4}$ to $6.35\cdot10^{-4}$ $\mathrm{mol\cdot kg^{-1}}$ and total chloride concentrations from $5.86\cdot10^{-4}$ to $3.26\cdot10^{-1}$ $\mathrm{mol\cdot kg^{-1}}$. The solutions were prepared by dissolving Palladium (II) Chloride, 99.9%, Reagent grade sodium chloride (ACP), and Optima® grade hydrochloric acid (Fisher Scientific) in Nanopure® de-ionized water. The $\mathrm{pH}^{25^\circ C}$ of the experimental solutions ranged from 1.92 to 3.22. In order to prevent formation of Pd (IV) species, the experimental solutions were stored in contact with metallic Pd under a nitrogen atmosphere. Traces of oxygen, which may result in formation of Pd (IV) species at elevated temperature, were removed by pumping the solutions through a HP 1050 Degasser (on line) prior to pumping them into the cell. After being pumped through the cell, the experimental solutions were collected for analysis of their total Pd and Cl concentrations using the neutron activation method at Ecole Polytechnique (Montreal).

To correct the spectra for background absorption, the absorption of the cell filled with Nanopure® de-ionized water was recorded before each of the Pd spectrum was collected. An estimate of the error of the measured absorption values was obtained from repeated measurements (several sets of 5 to 10 scans at each temperature) of the spectra of a solution having a total Pd concentration of $3.95\cdot10^{-4}$ $\mathrm{mol\cdot kg^{-1}}$. It was found that the absorption values were reproducible to a tolerance varying from 0.010 to 0.030 at 25 and 100 °C, and from 0.020 to 0.030 at higher temperatures.

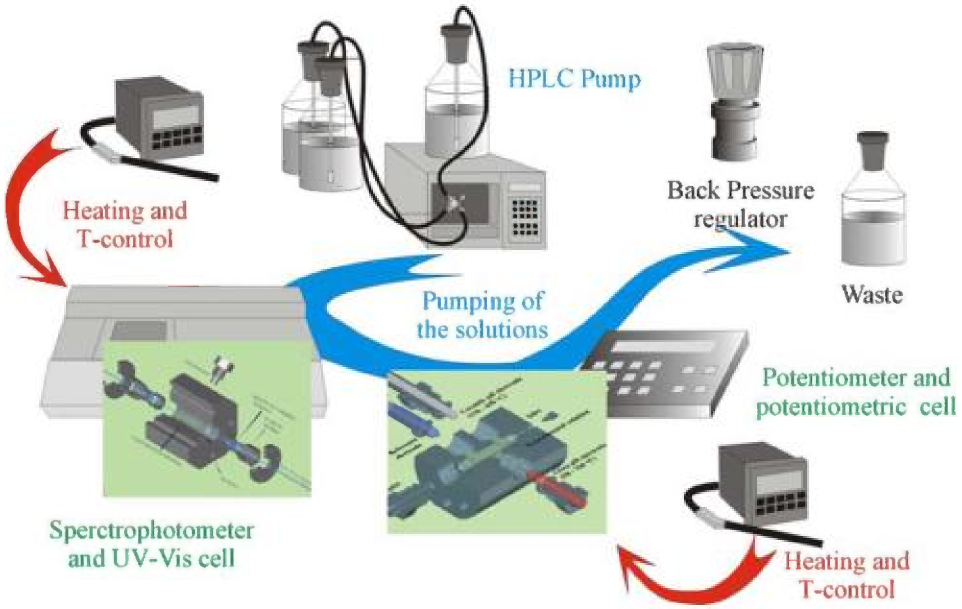

Figure 1. Drawing of the experimental system used in this study.

3. RESULTS

3.1 Speciation model

Some typical 25 °C absorbance spectra for chloride solutions of variable pH and Cl/Pd ratio are shown in Figure 2. From this figure it is evident that the spectra change significantly with variations in the Pd/Cl ratio, which indicates that there were changes in the coordination of Pd^{2+}. Temperature also affects the spectra, i.e., there is a red shift and associated decrease in absorbance with increasing temperature. However, the steep portion of the intense, chloride ion absorption edge in the spectral region below 210-220 nm overlaps with the Pd(II) chloride spectra at high temperature impeding visual identification of their absorbance peaks and makes it impossible to attribute specific spectral regions to absorbance of particular Pd complexes. In order to develop a chemical model for the solutions investigated and to determine the number of absorbing Pd(II) species, we used the method of absorbance matrix analysis described by Suleimenov and Seward (2000) and employed previously by us in a study of Nd speciation in chloride-bearing solutions (Migdisov and Williams-Jones, 2002).

In accordance with Beer's law and assuming a conventional linear model with respect to chemical composition, each of the experimental measurements at any given wavelength is defined by

$$\frac{A}{l} = \varepsilon_1 \cdot M_1 + \varepsilon_2 \cdot M_2 + ... + \varepsilon_n \cdot M_n \qquad (1),$$

where A is absorbance, ε_n is the molar extinction coefficient (or molal absorption coefficient) of the corresponding species, l is the pathlength, and M_n is the molar concentration of the corresponding species. As absorbance is a linear function of the composition of the solution, the maximum number of linearly independent columns in the absorbance matrix gives the number of absorbing species at the temperature investigated. If no two species have the same molar extinction coefficients, this number can be found by determining the rank of the absorbance matrix. As the experimentally determined uncertainties in the absorption values varied from 0.010 to 0.030 at 25 and 100 °C, and from 0.020 to 0.030 at higher temperature, the results of the rank calculations for these tolerance intervals were taken as the total number of absorbing species. At a tolerance of 0.035, the rank of the absorption matrix changes from 7 at 25 °C to 6 at 250°C, whereas in the tolerance range of 0.025 – 0.03 the calculated rank changes from 8 at 25 °C to 6 at 250°C. The results of the rank calculations show that the total number of absorbing species, including Cl, varies from eight at 25 °C to six at 250 °C.

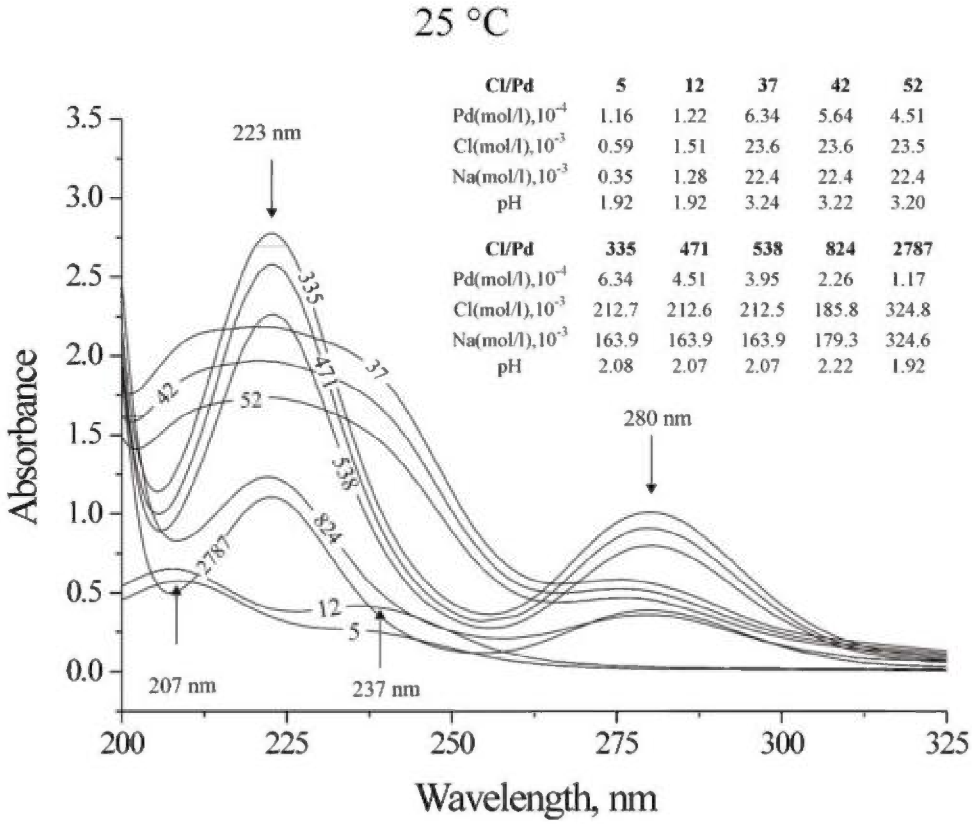

Figure 2. Examples of typical spectra corrected for solvent and window absorbance for chloride solutions of variable pH and Cl/Pd ratio at 25 °C.

Owing to the initial composition of the experimental solutions all of the speciaion models employed in this study contain Pd^{2+} and Cl^-, but Na^+ was omitted as the ion transparent in both visible and UV spectral regions. The rest of the absorbing species were selected based on speciation models published in the literature. Selecting the species for a model involving six absorbing species is straightforward as the simple chloride complexes $PdCl^+$, $PdCl_2°$, $PdCl_3^-$, $PdCl_4^{2-}$, have been described by many authors as being those dominant under acidic conditions (e.g., Sassani and Shock, 1998). However, in addition to the simple chlorides, Pd(II) is also known to form hydroxy- and hydroxychloride species in Cl-bearing aqueous solutions. Among these $PdCl_3(OH)^{2-}$ and $Pd(OH)_2°$ are the most important (e.g., Tait et al., 1991), and are even dominant under near-neutral conditions by Middlesworth and Wood (1999). In view of this, the eight species required to model the speciation for 25 °C were assumed to comprise Pd^{2+}, $PdCl^+$, $PdCl_2°$, $PdCl_3^-$, $PdCl_4^{2-}$, $PdCl_3(OH)^{2-}$, $Pd(OH)_2°$ and Cl-; the 100 °C isotherm was modeled using Pd^{2+}, $PdCl^+$, $PdCl_2°$, $PdCl_3^-$, $PdCl_4^{2-}$, $PdCl_3(OH)^{2-}$, and Cl^-; and the simple chloride speciation model was used for temperatures above 100 °C (Pd^{2+}, $PdCl^+$, $PdCl_2°$, $PdCl_3^-$, $PdCl_4^{2-}$, and Cl^-).

3.2 Calculation of the formation constants

Equilibrium constants were calculated for the following reactions:

$$Pd^{2+} + Cl^- = PdCl^+ \quad \beta 1,0 \quad (2);$$

$$Pd^{2+} + 2 \cdot Cl^- = PdCl_2^o \quad \beta 2,0 \quad (3);$$

$$Pd^{2+} + 3 \cdot Cl^- = PdCl_3^- \quad \beta 3,0 \quad (4);$$

$$Pd^{2+} + 4 \cdot Cl^- = PdCl_4^{2-} \quad \beta 4,0 \quad (5);$$

$$Pd^{2+} + 2 \cdot OH^- = Pd(OH)_2^o \quad \beta 0,2 \quad (6);$$

$$Pd^{2+} + OH^- + 3 \cdot Cl^- = PdCl_3OH^{2-} \beta 3,1 \quad (7).$$

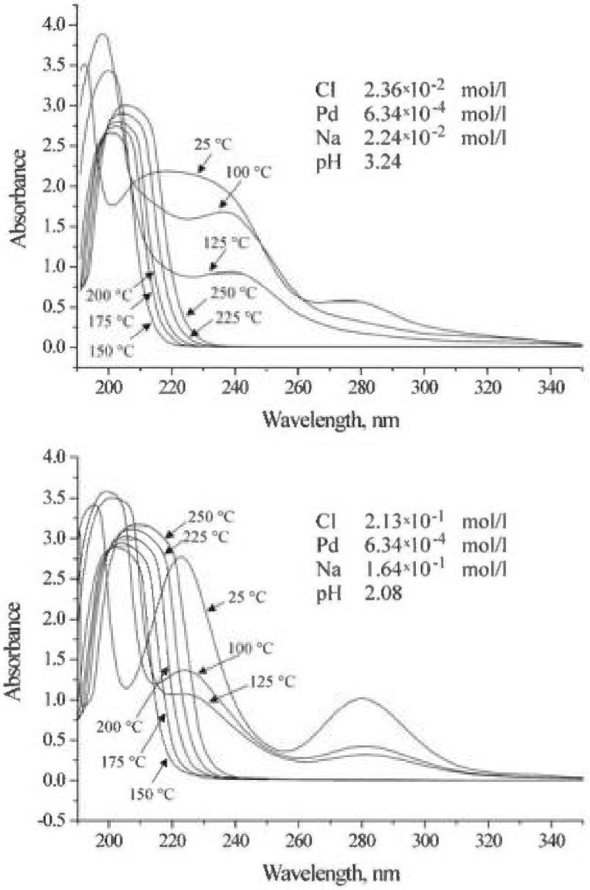

Figure 3. Examples of the spectra for Palladium chloride solutions with a total concentration of palladium of $6.34*10^{-4}$ mol/kg and variable concentrations of chloride ion at temperatures ranging from 25 to 250 °C (the measurements were made using a cell with a path length of 0.98 cm.)

The individual ion activity coefficients were calculated using the extended Debye-Hückel equation (Helgeson, 1981):

$$\log \gamma_n = \frac{A \cdot [z_n]^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + GAMMA + b_\gamma \cdot I \quad (8),$$

where GAMMA is the mole fraction to molality conversion (GAMMA =-log(1+0.0180153)), I is the ionic strength, A and B are the molal Debye-Huckel coefficients (Helgeson and Kirkham;1974), and b_γ represents the extended term for NaCl-dominated solutions (Helgeson et al., 1981; Oelkers and Helgeson, 1990). Following Kielland (1937) values for a (distance of closest approach) were taken as 3.5 Å for OH- and Cl-, and for palladium species were set at 4.5 Å. Given that Pd concentrations in the experimental solutions never exceeded $6.35 \cdot 10^{-4}$ mol·kg-1 and, thus, were too low to significantly influence pH, values of pH at the temperatures of the experiments were calculated as for NaCl-HCl system (Sverjensky et al., 1997)

In order to calculate the cumulative formation constants for the reactions (2-7) we used the method described by Suleimenov and Seward (2000) and Migdisov and Williams-Jones (2002). Arbitrarily selected initial values of the formation constants were refined iteratively by minimizing the function:

$$U = \sqrt{\sum_{i=1}^{I} \left[\sum_{k=1}^{K} \left(A_{ik}^{obs} - A_{ik}^{calc} \right)^2 \right]} \quad (9),$$

where i is the wavelength, I is the total number of wavelengths at which measurements were made, and K is the number of solutions. The variable A_{ik}^{calc} is the calculated absorbance, and is a function of the concentrations of the absorbing species and their molar extinction coefficients (see Eq. 1), whereas A_{ik}^{obs} is the absorbance determined experimentally. The calculations involved several cycles of iteration, which minimized U (Eq. 9) with respect to the formation constants. Only wavelength intervals in which peaks were detected were considered in the calculations. A peak was interpreted when the difference between the background absorbance and that of the solution reached 0.1 absorption units.

4. DISCUSSION

In the temperature interval 25-250° C, the values of the cumulative formation constants determined in this study are close (with ~ half a log unit) to those extrapolated from low temperature data by Wood et al. (1992) using the isocoulombic reaction approach (Figure 4). However, the values of log β4,0 determined in this study for temperatures above 200° C are higher those estimated by Wood et al. (1992), and diverge from the latter with increasing temperature. They are also higher than those determined experimentally by Gammons et al. (1992), although the rate of increase with increasing temperature for the two sets of data is similar.

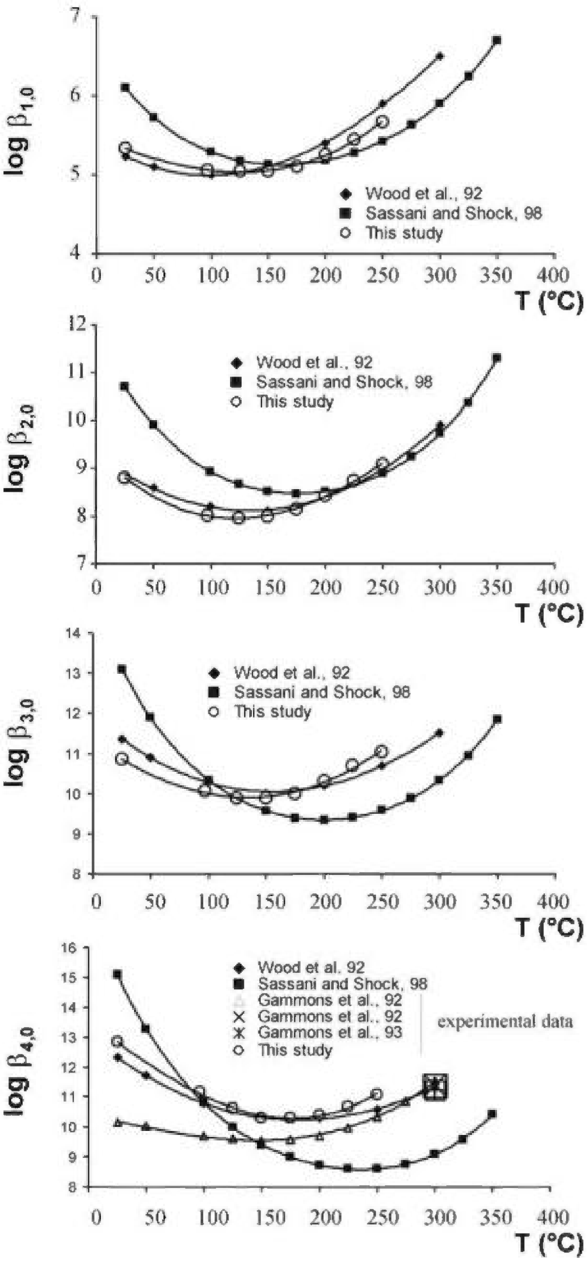

Figure 4. A series of diagrams showing the variation in the cumulative formation constants for $PdCl_n^{2-n}$ species with respect to temperature at saturated water vapor pressure.

By contrast, our values of the cumulative formation constants are substantially different from those calculated by Sassani and Shock (1998). The predicted log $\beta_{n,0}$ (n=1 to 4) of Sassani and Shock (1998) are significantly higher than those determined in this study or estimated by Wood et al. (1992) at temperatures below 100° C but at higher temperature increase more slowly in this study or estimated by Wood et al. (1992). At 250° C values of log $\beta_{4,0}$ are ~ 2.5 log units lower than those reported here.

As already discussed by Wood et al. (1992) and Gammons et al. (1992), the most important factors controlling the precipitation of palladium metal from acidic and relatively oxidizing chloride-bearing solutions at temperatures below 300° C are neutralization, dilution and reduction of a fluid as suggested by the reaction

$$Pd^{cryst} + 2H^+ + 4Cl^- + 0.5O_2^{gas} = PdCl_4^{2-} + H_2O$$

In order for there to be significant transport of palladium in the temperature range 25-300 °C, very high salinities (e.g., NaCl-saturated brines at 25°C), and unusually low pH (pH<3-4, e.g., fluids capable of inducing argillic alteration in feldspar-rich rocks), and oxidizing conditions (well into the stability field of hematite) are required. However, if the data are extrapolated to temperatures above 300° C, it is evident from Figure 5 that similar solubility levels are possible under much less acidic and more reducing conditions.

The results of our study support the conclusion of Xiong (1999) and Xiong and Wood (2000) that significant concentrations of Pd (tens of ppb) may be transported as chloride complexes between 400-500° C and 550 bars in hydrothermal solutions of ionic strength ~ 0.1, at a pH buffered by muscovite+quartz+K-feldspar (pH 5 to 5.5) and at an oxygen fugacity corresponding to Re+ReO_2 (~ 1.5 log unit below the hematite-magnetite buffer) or MnO+Mn3O4. It must be remembered however that the above conclusions on the solubility of palladium apply only to the case where the corresponding solid is metal palladium. If palladium were present in the form of an alloy or as a sulfide, telluride, selenide or bismuthide (for which the stability relative to palladium metal with respect to fO_2 and pH would depend on the activity of S-Te-Se-Bi in the solution), the solubility would be lower as these phases are less soluble than palladium metal (see Wood et al., 1992; Gammons and Bloom, 1993; Pan and Wood, 1994).

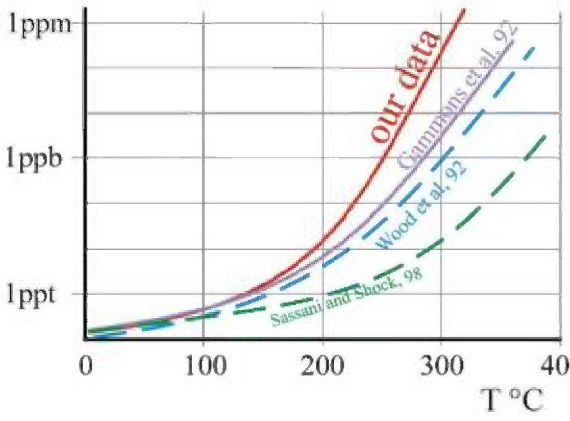

Figure 5 The solubility of metallic palladium in a 1 molal solution of NaCl (pH=2)

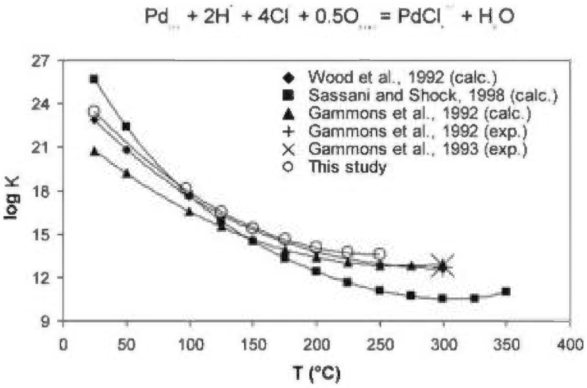

Figure 6 Diagram illustrating the variation in the value of log K for reaction (12) as a function of temperature at saturated water vapor pressure

5. CONCLUSIONS

The values of the cumulative formation constants determined in this study are close to those extrapolated from low temperature data by Wood et al. (1992), and diverge sharply from those predicted using the correlation methods of Sassani and Shock (1998). Most importantly, they show that $PdCl_4^{2-}$, $PdCl_3^-$ and $PdCl_2^o$ are significantly more stable at elevated temperatures than was previously thought, and that above 400 °C, the solubility of Pd in chloride-bearing aqueous solutions is high enough for the latter to constitute viable ore fluids. This project has provided the first reliable experimental data at elevated temperatures for the mobilization and concentration of Pd by hydrothermal fluids and in so doing, has furnished some of the basic information required to develop genetic models for the formation of hydrothermal deposits of palladium.

REFERENCES

Baes C. E., Mesmer R. E. (1976) The Hydrolysis of Cations. J. Wiley and Sons.
Barnes, S.-J., Maier, W.D. (2002). J. Petrol., 43, 103-128.
Biryukov A. A., Shlenskaya V. L. (1964). Russian J. Inorg. Chem. 9,450-452.
Boudreau, A.E. (1995). Explor. Min. Geol., 4, 215-225.
Byrne R. H., Yao W. (2000) Geochim. Cosmochim. Acta 64, 4153–4156.
Cosden, J.M., Byrne, R.H., (2003) Geochim. et Cosmochim. Acta, 67, 1331–1338
Droll, H.A.; Block, B. P.; Fernelius, W. C.. (1957) Journal of Physical Chemistry, 61, 1000-4
Elding L. I. (1972) Inorg. Chim. Acta 6, 647–651.
Farrow, C.E. G., Watkinson, D.H.. (1997) Canadian Mineralogist, 35(4), 817-839.
Gammons, C. H. (1995) Geochim. et Cosmochim. Acta, 59, 1655-1667.
Gammons, C. H., Bloom, M. S. (1993) Geochim. et Cosmochim. Acta, 57, 2451-2467.
Gammons, C. H., Bloom, M. S., Yu, Y. (1992) Geochim. et Cosmochim. Acta, 56, 3881-3894.
Gammons, C. H., Yu, Y., Bloom, M. S. (1993) Geochim. et Cosmochim. Acta 57, 2469-2479.
Helgeson, H.C., Kirkham, D.H.. (1974) American Journal of Science, 274, 1199-261
Helgeson, H.C., Kirkham, D.H., Flowers, G.C. (1981) American Journal of Science, 281, 1249-516.
Helmy, H.M., Stumpfl, E.F., Kamel, O.A. (1995) Econ. Geol., 90, 2350-60.
Hsu, L.C., Lechler, P.J., Nelson, J.H. (1991). Econ. Geol., 86, 422-427.
Izatt, R.M., Eatough, D., Christensen, J.J. (1967) Journal of the Chemical Society [Section] A: Inorganic, Physical, Theoretical, 8, 1301-4
Kielland J. (1937) J. Amer. Cem. Soc., 59, 1675-1678
Liu, W., McPhail, D.C., Brugger, J. (2001) Geochim. et Cosmochim. Acta, 65 (17), 2937-2948
McKibben, M.A., Williams, A.E., Hall, G.E. (1990) Econ. Geol., 85, 1926-34.
Middlesworth J. M., Wood S. A. (1999) Geochim. Cosmochim. Acta, 63, 1751–1765.
Migdisov, Art.A., Williams-Jones, A.E. (2002) c Geochim. Cosmochim. Acta, 66 (24), 4311 - 4323
Li, C., Naldrett, A. J.. (1993) Econ. Geol., 88(7), 1780-96.
Oelkers, E.H., Helgeson, H.C.. (1990) Geochimica et Cosmochimica Acta, 54(3), 727-38
Orlova G. P., Ryabchikov I. D., Distler V. V., Gladyshev, G. D. (1987) Int. Geol. Rev. 29, 360-362.
Pan, P., Wood, S. A. (1994) Mineralium Deposita 29, 373-390.
Ripley, E.M., Chryssoulis, S.L.. (1994) Econ. Geol., 89, 201-10.

Sassani, D. C., Shock, E. L. (1998) Geochimica et Cosmochimica Acta 62, 2643-2671.

Suleimenov, O. M., Seward, T. M. (2000) Chem. Geol., 167(1-2), 177-192.

Sverjensky, D. A., Shock, E. L., Helgeson, H. C. (1997) Geochim. et Cosmochim. Acta, 61, 1359-1412

Tait, C. D., Janecky, D. R., Rogers, P. S. Z. (1991) Geochimica et Cosmochimica Acta 55, 1253-1264.

Werle, J.L., Ikramuddin, M., Mutschler, F.E. (1984) Canadian Journal of Earth Sciences, 21(6), 630-41.

Wood, S. A., Mountain, B. W., Pan, P. (1992) Canadian Mineralogist 30, 955-982.

Xiong, Y., Wood, S. A. (2000) Mineralogy and Petrology 68, 1-28.

Xiong, Y. (1999) Experimental study of the solubility of rhenium, osmium and palladium in subcritical and supercritical KCl solutions to 500 degrees C. M.Sc. Thesis, University of Idaho, 224 p.