

Experimental quantification of hydrothermal solubility of platinum-group elements with special reference to porphyry copper environments

Y. Xiong* and S. A. Wood

Laboratory for Experimental Aqueous Geochemistry, Department of Geology and Geological Engineering, University of Idaho, Moscow, ID, U.S.A.

With 3 Figures

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Summary

We have conducted a series of experiments on the solubility of metallic osmium and palladium in supercritical aqueous KCl fluids in which pH was buffered by the assemblage K-feldspar-quartz-muscovite and oxygen fugacity was controlled by various oxygen buffers at 400° and 500°C. An important objective of these well-constrained experiments is to evaluate current theoretical models of PGE solubility.

Our experimental results indicate that the concentration of Os in a 1.0 m KCl solution buffered by the Ni-NiO (NNO) assemblage at 500°C is ~3 ppb ($\sim 1.9 \times 10^{-8}$ moles/kg H₂O), whereas the concentration of Os in a 1.5 m KCl solution also buffered by NNO at 500°C is ~130 ppb ($\sim 6.5 \times 10^{-7}$ moles/kg H₂O). As the pH in these two experiments is nearly the same, this finding implies that Os is present in solution as a chloride complex. The concentration of Os in a 1.5 m KCl solution but buffered by a higher oxygen fugacity buffer (Re-ReO₂ assemblage) (RRO) is about one order of magnitude higher (~1705 ppb; $\sim 1 \times 10^{-5}$ moles/kg H₂O).

The palladium concentrations in a 0.1 m KCl solution buffered by RRO at 500°C and in a 0.1 m KCl solution buffered by MnO-Mn₃O₄ at 400°C are ~40 ppb ($\sim 3.8 \times 10^{-7}$ moles/kg H₂O) and ~15 ppb (1.4×10^{-7} moles/kg H₂O), respectively. Our experimental results on the solubility of Pd metal in combination with field observations show that the theoretical calculations of *Sassani* and *Shock* (1990, 1998)

* Present address: Department of Geological Sciences, Wright Laboratories, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854-8066, U.S.A

on palladium underestimate the solubility of palladium by many orders of magnitude under supercritical conditions.

Our experimental results are directly applicable to porphyry copper systems because in such systems temperature, pH, salinity and oxygen fugacity are similar to the experimental parameters. Application of our experimental results indicate that a typical porphyry systems can transport at least 40 tons of Pd if sources of platinum-group elements (PGE) are available and the solubility-controlling phase is metallic Pd. Similarly, the amount of osmium that can be transported in a typical porphyry system is calculated to be at least ~ 3 tons. Consequently, porphyry systems have the capacity to transport sufficient PGE to form at least mid-sized PGE deposits. The absence of important Os mineralization in known porphyry deposits may be due to the lack of availability of source materials, or to the presence of Os in less soluble forms, such as sulfides.

Zusammenfassung

Experimentelle Bestimmung der hydrothermalen Löslichkeit von Platingruppen-Elementen unter besonderer Berücksichtigung von Porphyry Copper-Systemen

Wir haben eine Reihe von Experimenten zur Löslichkeit von metallischem Osmium und Palladium in überkritischen wässrigen KCl Fluiden durchgeführt. Dabei war pH durch die Assoziation K-Feldspat-Quarz-Muskovit gepuffert, die Sauerstoff-Fugazität wurde durch verschiedene Sauerstoffpuffer bei 400 und 500 °C kontrolliert. Ein wichtiges Ziel dieser sorgfältig eingegrenzten Experimente war es, die derzeit bestehenden theoretischen Modelle zur PGE-Löslichkeit zu testen.

Unsere experimentellen Ergebnisse zeigen, dass die Konzentration von Osmium in einer 1,0 m KCl-Lösung mit Ni-NiO (NNO) Puffer bei 500 °C ungefähr 3 ppb ($\approx 1,9 \times 10^{-8}$ mol/kg H₂O) beträgt, wogegen die Konzentration von Osmium in einer 1,5 m KCl-Lösung, auch durch NNO bei 500 °C gepuffert, bei ≈ 130 ppb ($\approx 6,5 \times 10^{-7}$ mol/kg H₂O) liegt. Dass der pH in beiden Experimenten fast identisch ist, weist darauf hin, dass Osmium in der Lösung als Chloridkomplex vorliegt. Die Konzentration von Osmium in einer 1,5 m KCl-Lösung, aber mit einem Puffer mit höherer Sauerstoff-Fugazität (Re-ReO₂) (RRO) gepuffert, ist ungefähr um eine Größenordnung höher (≈ 1705 ppb; $\approx 1 \times 10^{-5}$ mol/kg H₂O).

Die Palladium-Konzentration in einer 0,1 m KCl-Lösung, die durch RRO bei 500 °C gepuffert wird, und in einer 0,1 m KCl-Lösung, die bei 400 °C durch MnO-Mn₃O₄ gepuffert wird, sind 40 ppb ($\approx 3,8 \times 10^{-7}$ mol/kg H₂O) und ungefähr 15 ppb ($1,4 \times 10^{-7}$ mol/kg H₂O).

Unsere experimentellen Ergebnisse zur Löslichkeit von Palladium-Metall zeigen, zusammen mit Geländebeobachtungen, dass die theoretischen Berechnungen von *Sassani* und *Shock* (1990, 1998) die Löslichkeit von Palladium unter superkritischen Bedingungen um viele Größenordnungen unterschätzen.

Dies lässt sich direkt auf Porphyry Copper-Systeme anwenden, weil in diesen Temperaturen, pH, Salinität und Sauerstoff-Fugazität den experimentellen Parametern weitgehend entsprechen. Die Anwendung unserer experimentellen Ergebnisse zeigt, dass ein typisches Porphyry Copper-System mindestens 40 t Palladium transportieren kann, wenn Quellen von Platingruppen-Elementen (PGE) verfügbar sind und wenn die Phase, die die Löslichkeit kontrolliert, metallisches Pd ist. In ähnlicher Weise lässt sich die Menge von Osmium, die in einem typischen Porphyry-System transportiert werden kann, mit mindestens 3 t berechnen. Porphyry-Systeme sind somit in der Lage, ausreichend PGE zu transportieren, um zumindest PGE-Lagerstätten mittlerer Größe zu erzeugen. Das Fehlen von bedeutendem Osmium-Mineralisation in bekannten Porphyry-Lagerstät-

ten lässt sich entweder auf das Fehlen geeigneter Metallquellen, oder auf die Anwesenheit von Osmium in weniger löslicher Form, wie z.B. als Sulfid, zurückführen.

Introduction

Osmium and other platinum-group elements (PGE) have traditionally been considered to be immobile under geologically reasonable hydrothermal conditions and to be transported and concentrated by magmatic processes (*Naldrett and Duke, 1980; Barnes and Naldrett, 1985; Cawthorn and Barry, 1992*). However, at least four observations imply the mobility of PGE, including Os, under hydrothermal conditions. First, a number of PGE deposits exhibit characteristics suggesting that hydrothermal fluids were involved in their formation (*Wilde et al., 1989; Ohnenstetter et al., 1991; Watkinson and Melling, 1992; Watkinson and Ohnenstetter, 1992; Mernagh et al., 1994; McDonald et al., 1995*). Second, open-system behavior of the Re-Os system has been documented in case studies (*Walker et al., 1989; Marcantonio et al., 1994; Lambert et al., 1998*). Third, platinum-group minerals (such as merenskyite (PdTe₂), kotulskite (PdTe) and moncheite (PtTe₂)) have been observed in typical porphyry copper deposits in the Philippines and elsewhere (*Tarkian and Koopmann, 1995; Tarkian, 1998*), and considerable amounts of PGE are associated with porphyry copper deposits in the western United States and Canada (e.g. *Werle et al., 1984; Mutschler et al., 1985; Bonham, 1989; Lechler, 1995*), and in Greece (*Eliopoulos and Economou-Eliopoulos, 1991*). Fourth, high concentrations of PGE in hydrothermal minerals and ores suggest that hydrothermal fluids must have played a role in the transport of PGE. For instance, compared with 0.03–0.05 ppb Os, 0.4–2.0 ppb Pd and 0.4 ppb Pt in the crust (*Taylor and McLennan, 1985, 1995; Wedepohl, 1995; Schmidt et al., 1997*), elevated concentrations of PGE have been observed in sulfides (Os, up to 3.99 ppb) from modern seafloor hydrothermal systems (*Ravizza et al., 1996*), in pyrite, chalcopyrite and pyrrhotite (Os, up to 0.77 ppb; Pd, 27 ppb; Pt, 300 ppb) from the porphyry copper and skarn deposits as well as in ores (Os up to 24 ppb) of skarn deposits in China (*Chang et al., 1991*).

In attempts to quantify the mobility of PGE (mainly Pt and Pd) in hydrothermal solutions, theoretical calculations have been conducted (*Mountain and Wood, 1988; Wood et al., 1989, 1992; Sassani and Shock, 1990; Jaireth, 1992; Sassani and Shock, 1998*). The calculations of *Wood* and colleagues on Pt and Pd and of *Jaireth* on Pt are for temperatures up to 300 °C, whereas those of *Sassani and Shock* on Pd are for temperatures up to 1000 °C. The former calculations provide useful information on the transport and deposition mechanisms of Pt and Pd under lower temperature hydrothermal conditions in various environments, including unconformity-type uranium deposit environments. However, even though the calculations of *Sassani and Shock* (1990, 1998) extend to 750 °C and 1000 °C, respectively, their conclusions should be treated with caution because, as discussed in detail by *Wood et al. (1992)*, the data of *Droll et al. (1957)* for 25 °C used by *Sassani and Shock* (1990, 1998) as the basis of their extrapolations may be in error.

Along with theoretical calculations, a few experimental studies have been conducted to assess the solubility of Pt and Pd phases. *Orlova et al. (1987)* investigated the solubility of Pt metal at 600 °C in NaCl and KCl solutions, and

Hsu et al. (1991) measured the solubility of Pd metal from 300° to 700°C in chloride solutions. Most recently, *Likhoidov et al.* (1998) studied the solubility of metallic Pt from 300° to 500°C in chloride solutions in the presence of various manganese oxide buffers. However, the results from these experimental studies are difficult to interpret and the findings are inconclusive because important variables such as pH and/or f_{O_2} were not controlled. In the lower temperature range up to 350°C, there are well-constrained experimental results on the solubility of Pt and Pd sulfides in sulfide solutions (*Gammons and Bloom*, 1993; *Pan and Wood*, 1994; *Wood et al.*, 1994) and in NaCl/sulfate solutions (*Gammons et al.*, 1992), and on the solubility of Ag-Pd alloy in chloride solutions (*Gammons et al.*, 1993). These studies suggested that bisulfide complexes of Pt and Pd are important in remobilization of Pt and Pd over a wide range of pH, under reducing conditions, at geologically reasonable sulfide concentrations. Under unusually oxidizing (e.g. the Mn_3O_4 - Mn_2O_3 buffer) and low-pH conditions, chloride complexes are important, because concentrations of dissolved Pt and Pd as chloride complexes can be greater than 1 ppm (*Gammons et al.*, 1992, 1993).

The brief review above shows that, although a consistent picture on the solubility of Pt and Pd below 350°C has emerged owing to advances in experimental and theoretical approaches, reliable data are still lacking on the solubility of PGE at higher temperatures (e.g. 500°–600°C), typical of magmatic hydrothermal fluids possibly responsible for the transport of PGE in porphyry systems, and the enrichment of PGE in classic PGE ore deposits such as the Duluth and Stillwater Complexes. More importantly, we are aware of no experimental data on the solubility of Os in hydrothermal fluids. Quantification of the hydrothermal transport of osmium under various conditions is essential to more fruitful applications of the Re-Os radiogenic system and for the better understanding of the genesis of PGE deposits with disputed origins.

To quantify the hydrothermal transport of PGE, and the possible conditions thereof, we have conducted experimental studies on the solubility of Os under hydrothermal conditions with supplemental studies on the solubility of Pd. In this communication, we report our experimental results on the solubility of Os and Pd in supercritical aqueous KCl solutions under controlled conditions. In addition to providing PGE solubility data in environments directly relevant to porphyry systems and providing guidance to future experimental investigations, an important objective of these well-constrained experiments is to assess theoretical calculations based on the models of *Sassani and Shock* (1990, 1998). It should be pointed out that, although we have not derived thermodynamic data from the present study, our experiments represent the first step towards quantification of the geochemical behavior of PGE under supercritical conditions and clearly place some constraints on the amount of Os and Pd that can be transported under such conditions.

Methodology

In our experiments, self-sealing reaction vessels with a volume of approximately 250 mL, lined with gold, and which permit withdrawal of samples at temperatures and pressures of interest, were used. The pH and f_{O_2} were buffered by thermodynamically well-characterized solid phase assemblages such as K-

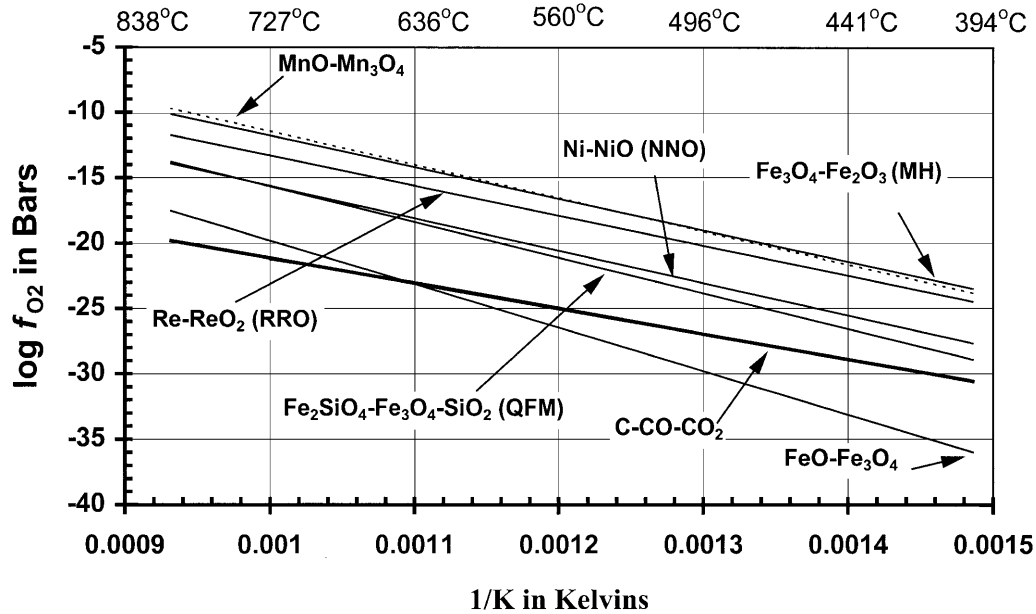


Fig. 1. $\log f_{O_2}$ – T path of various oxygen fugacity buffers in different environments in the temperature range from 400° to 800° C. Oxygen fugacities of FeO-Fe₃O₄ (WM), Ni-NiO (NNO), MnO-Mn₃O₄, Fe₃O₄-Fe₂O₃ (MH) and quartz-fayalite-magnetite (QFM) are calculated from the equations of *Chou* (1987). $\log f_{O_2}$ values for the C (graphite)-CO-CO₂ buffer are from *French and Eugster* (1965) where $P_{\text{gas}} = 1$ bar. $\log f_{O_2}$ values for the Re-ReO₂ (RRO) buffer are calculated from *Pownceby and O'Neil* (1994). The Re-ReO₂, MnO-Mn₃O₄ and Ni-NiO buffers were used in our experiments. For reference, QFM, NNO, WM, and C-CO-CO₂ buffers are relevant to mafic and ultramafic environments, whereas MH and MnO-Mn₃O₄ buffers are relevant to porphyry systems

feldspar + muscovite + quartz (*Sverjensky et al.*, 1991), Re-ReO₂ (*Pownceby and O'Neil*, 1994), and Ni-NiO (*Chou*, 1987) (Fig. 1). K-feldspar, quartz, and muscovite were mixed in approximately a 1:1:1 mass ratio and the total mass was approximately 15 grams. Natural K-feldspar, quartz, and muscovite were purchased from WARD'S Natural Science Establishment, Inc. The K-feldspar is from Madawaska, Ontario, Canada, the quartz is from Minas Gerais, Brazil, and the muscovite is from Stoneham, Maine. The latter was determined to be close to the pure muscovite end-member (*Woodard*, 1951). Our X-ray diffraction data corroborate this conclusion, as the Na/(Na + K) atom ratios calculated from the d(002)-spacing employing the equation of *Guidotti* (1984) are less than 5%. K-feldspar was purified by heating 1:1 mixtures of KCl and K-feldspar at 700° C for approximately 90 days. In all experiments, Os (purity 99.9%, minimum grain size $\geq 1.8 \mu\text{m}$, Aldrich Chemical Company) metal powder and the oxygen fugacity buffer assemblage were loaded into gold or silver capsules. Then the capsules were crimped, but not welded, at both ends. Palladium foil (purity 99.9%, Johnson Matthey Company) was used in experiments investigating palladium solubility. In one experiment, OsO₂ (s) was used as a starting material.

The components of the oxygen fugacity buffers, MnO (99%, grain size smaller than 250 μm , larger than 88 μm), Mn₃O₄ (97%, grain size smaller than 44 μm ,

minimum grain size $\geq 1.8 \mu\text{m}$), Re (99.995%, grain size smaller than $149 \mu\text{m}$, minimum grain size $\geq 1.8 \mu\text{m}$), and ReO_2 (99.9%, grain size smaller than $44 \mu\text{m}$, minimum grain size $\geq 1.8 \mu\text{m}$), are from Aldrich Chemical Company. The Ni (99.9%, grain size smaller than $53 \mu\text{m}$, minimum grain size $\geq 1.8 \mu\text{m}$) and NiO (99%, grain size smaller than $44 \mu\text{m}$, minimum grain size $\geq 1.8 \mu\text{m}$) are from Johnson Matthey Company.

Although native osmium is not a common mineral in PGE deposits, it does occur in the Uralian-type or Alaskan-type complexes such as the Yubdo complex in Ethiopia, the Guseva Gora-Kachkarar and Barancha complexes in the Ural folded region (Razin, 1976; Cabri, 1981a), the Konder complex in Far Eastern Russia (Cabri et al., 1998), and in the Witwatersrand reefs (Feather and Koen, 1975). Osmium also combines with other PGE to form natural alloys such as osmiridium (Cabri, 1981a,b). Native Os occurs along with laurite as inclusions in interstitial sulfides in the Zambales ophiolite complex in the Philippines (Bacuta et al., 1990). Native osmium is associated with clinopyroxenite-gabbro where Os is contained mainly in titanomagnetite ores (Razin, 1976). To supplement the experimental studies on osmium metal, additional experiments on the solubility of metallic Pd (Pd foil as starting material) in KCl solutions were conducted. In these experiments, f_{O_2} was buffered by Re- ReO_2 and MnO- Mn_3O_4 buffers. Although native palladium is not a common phase, its presence in the Uralian-type ultramafic complexes (Cabri, 1981a) and in sandstone copper deposits (Kucha, 1990; Piestrzynski and Sawlowicz, 1999) has been reported. Palladium also occurs as a Pd-rich Au mineral, porpessite, in some low temperature deposits (Gammons et al., 1993). Therefore, the use of metallic Os and Pd as starting materials is at least directly relevant to the behavior of PGE in the Uralian-type ultramafic complexes during the interactions between fluids and rocks. It is also likely that metallic Os and Pd may control PGE solubility in some environments where reduced sulfur is low in concentration or absent. Furthermore, once thermodynamic data have been derived from future experiments, the solubilities of other Os and Pd phases can be calculated, provided that thermodynamic data are available or can be estimated for the latter.

In addition, to assess the solubility of erlichmanite (OsS_2) in sulfur-containing environments, two experiments were conducted using erlichmanite as starting material. In these experiments, f_{O_2} and f_{S_2} were buffered by the magnetite-pyrite-pyrrhotite assemblage. Erlichmanite was synthesized using pure sulfur (99.998%, Aldrich Chemical Company) and osmium powder (99.9%, Aldrich Chemical Company). Sulfur and osmium powder were well mixed, with sulfur in slight excess according to the stoichiometry before loading into a silica tube. After loading the mixed powder into the silica tube, the silica tube was sealed and then placed into a furnace to be heated to 500°C for 12 hours and then to 600°C for 5 hours. The synthesized product has the exact X-ray patterns with erlichmanite.

After the reaction vessels were assembled into the furnaces, compressed argon was used to check for leaks in the line. Then the reaction vessels were purged with compressed argon at least three times to dislodge and remove any residual air in the reaction vessels. The vessels were then heated rapidly to the desired temperature and pressure in nichrome resistance furnaces. The amount of electric power provided to the top and bottom of the furnace could be adjusted separately so that the thermal gradient could be controlled precisely. The temperature was controlled

by a CN5001 digital temperature controller manufactured by Omega Engineering, Inc. at Stamford, Connecticut. The controller is connected with a K-type thermocouple that was installed in the furnace close to the heating elements. Before using the thermocouple, it was calibrated against an ice bath (0 °C) and the error was found to conform with company specifications. Temperature was measured using two external thermocouples; one at the top of the vessel and the other at the bottom. These two external thermocouples are connected with a DP460 temperature indicator from Omega Engineering, Inc. To homogenize the solutions in the vessel, convection was induced by maintaining the bottom of the vessel 2 °C higher than the top.

Pressure was measured to within ± 10 bars using a pressure transducer and a digital pressure meter from Omega Company. To minimize the exposure of the transducer to corrosion, the vessel was connected with an Ashcroft Inconel 718 tube analogue gauge in some experimental runs, and the pressure was measured to within ± 15 bars. Both the transducer and Ashcroft analogue gauge were calibrated against a Heise analogue gauge.

When sampling, supercritical conditions were assured by setting run temperatures and pressures according to the data of *Sourirajan* and *Kennedy* (1962) for the analogous NaCl system. The sampling technique is similar to that of *Bourcier* and *Barnes* (1987). The sample size was usually 3.0 to 6.0 grams of solution. Each sample was split into two aliquots, one of which was filtered through a 0.20- μm nylon filter and the other left unfiltered. Then both aliquots were acidified with 0.5 or 1.0 mL concentrated HCl and diluted to 5 mL or 10 mL. Samples of larger size (>10 grams) were acidified with 2.5 mL concentrated HCl and diluted to 25 mL. After each sampling, the reaction vessels were recharged with approximately the same amount of fluid as removed to maintain the pressure of interest.

The concentrations of Os and Pd were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with an axial-view torch (Perkin Elmer Optima 3000 XL). In order to minimize matrix effects, blanks and standard calibration solutions were precisely matched with the samples with respect to matrix. The correlation coefficients of the calibration curves were better than 0.999. A conservative detection limit for osmium and palladium is estimated to be close to 5 ppb based upon at least three replicate analyses of matrix-matched blanks. Some samples with lower Os concentrations were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) at Washington State University. The detection limit of the ICP-MS for Os is 0.01 ppb. In analyzing Os and Pd using ICP-AES, Rh was used as an internal standard. Bismuth was used as an internal standard in analyzing Os by ICP-MS. To monitor the quality of analyses, standards of known concentration were analyzed as samples after every 6 samples had been analyzed. The deviation from the known concentration was less than 10% in ICP-AES and less than 6% in ICP-MS. The analytical precision for ICP-AES in terms of the relative standard deviation (RSD) of replicate analyses is better than 4.9% for Os and 7.9% for Pd. The analytical precision for ICP-MS is better than 10%.

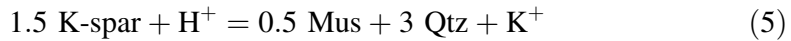
After each run, the starting phase(s), and the pH and f_{O_2} buffer assemblages were examined by X-ray powder diffraction. No components of the buffer were observed to be exhausted and no new phases appeared during any run, suggesting that buffered conditions were maintained.

Table 1. *Calculated molal concentrations of major species in the KCl-H₂O system*

pH	pOH	log m _{K⁺}	log m _{Cl⁻}	log m _{KCl⁰}	log m _{HCl⁰}	log m _{KOH⁰}
1.5 m KCl, 500 °C, 800 bars						
4.6	7.3	-0.4	-0.4	0.03	-1.6	-5.8
1.0 m KCl, 500 °C, 800 bars						
4.6	7.3	-0.6	-0.6	-0.1	-1.8	-5.8
0.5 m KCl, 500 °C, 550 bars						
5.5	7.6	-0.3	-0.3	-1.4	-2.8	-6.3
0.1 m KCl, 500 °C, 550 bars						
5.5	7.6	-1.4	-1.4	-1.2	-2.6	-6.3
0.1 m KCl, 400 °C, 550 bars						
5.0	6.3	-1.1	-1.1	-1.7	-4.1	-5.9

In order to facilitate the interpretation of experimental results, the pH values and molar concentrations of major species in the KCl-H₂O system at different KCl concentrations were calculated according to the following equations using the EQBRM computer code (*Anderson and Crerar, 1993*) (Table 1). Equilibrium constants for these reactions were obtained from the SUPCRT92 data base (*Johnson et al., 1992*) with updated parameters for relevant species for HKF equations from *Sverjensky et al. (1991)*; *Pokrovskii and Helgeson (1997)* and *Tagirov et al. (1997)*.

Mass-action expressions were:



Charge balance

$$m_{\text{H}^+} + m_{\text{K}^+} = m_{\text{Cl}^-} + m_{\text{OH}^-} \quad (6)$$

Mass balance

$$\begin{aligned} m_{\Sigma\text{Cl}} &= m_{\Sigma\text{K}} = m_{\text{Cl}^-} + m_{\text{KCl}^0} + m_{\text{HCl}^0} \\ &= m_{\text{K}^+} + m_{\text{KCl}^0} + m_{\text{KOH}^0} \end{aligned} \quad (7)$$

Activity coefficients for charged species are calculated using the extended Debye-Hückel equation (*Henley et al., 1984*),

$$\log \gamma_i = -A Z_i^2 I^{0.5} / (1 + a_i B I^{0.5}) + bI \quad (8)$$

where A and B at 400 °C and 0.5 kbar and 500 °C and 1 kbar are from *Helgeson* and *Kirkham* (1974), α is from *Nordstrom* and *Munoz* (1986), and b for the similar NaCl system is from *Helgeson et al.* (1981). Activity coefficients of neutral species are assumed to be unity.

The pH values fixed by the assemblage KMQ in our experiments in both 1.0 m and 1.5 m KCl solutions at 500 °C and 800 bars are calculated to be 4.6 (Table 1) (for reference, neutral pH at 500 °C and 800 bars is ~ 6.0). The pH of the KMQ buffer in 0.1 m KCl solution at 500 °C and 550 bars is calculated to be 5.5 (neutral pH at 500 °C and 550 bars is ~ 6.6) and in 0.1 m KCl solution at 400 °C and 550 bars is calculated to be 5.0 (neutral pH at 400 °C and 550 bars is ~ 5.6), respectively. Therefore, the experiments are all in the slightly acidic pH range.

Experimental results and interpretations

Osmium solubility experiments were conducted in 1.0 and 1.5 m KCl solutions at 500 °C under buffered pH and $\log f_{O_2}$ conditions. These results are plotted on Fig. 2 and tabulated in Table 2. Palladium solubility experiments were conducted in a 0.1 m KCl solution at 400° and 500 °C (Table 2 and Fig. 3). The average equilibrium concentrations for each experimental run are tabulated in Table 3. In calculating the average equilibrium concentrations of Os at 500 °C, all of the data

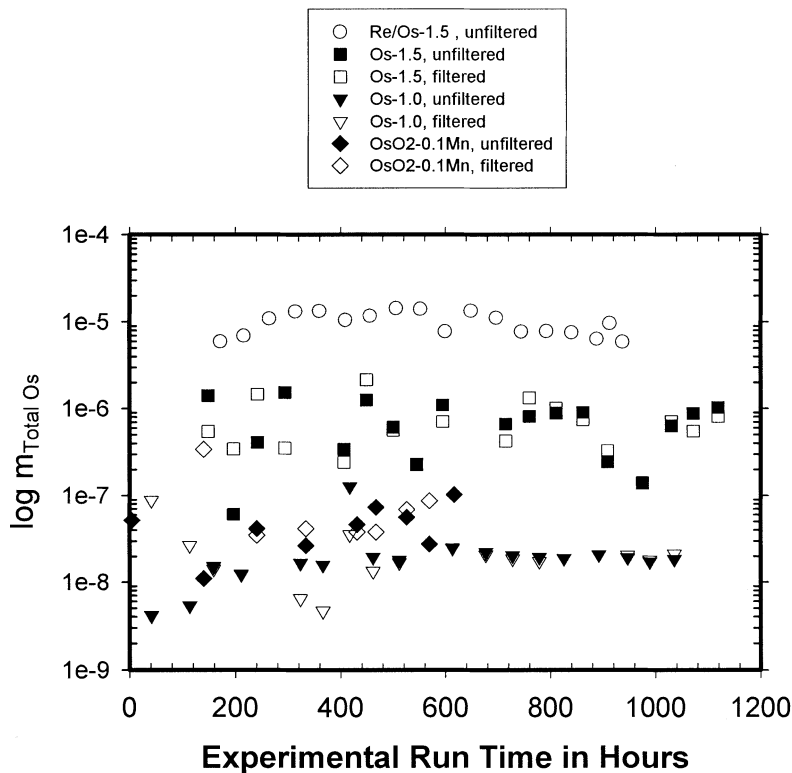


Fig. 2. Osmium concentrations from various experimental runs at 500 °C. Notice that for many of experiments equilibrium was closely attained after 200 hours. For all experiments equilibrium was attained after 450 hours

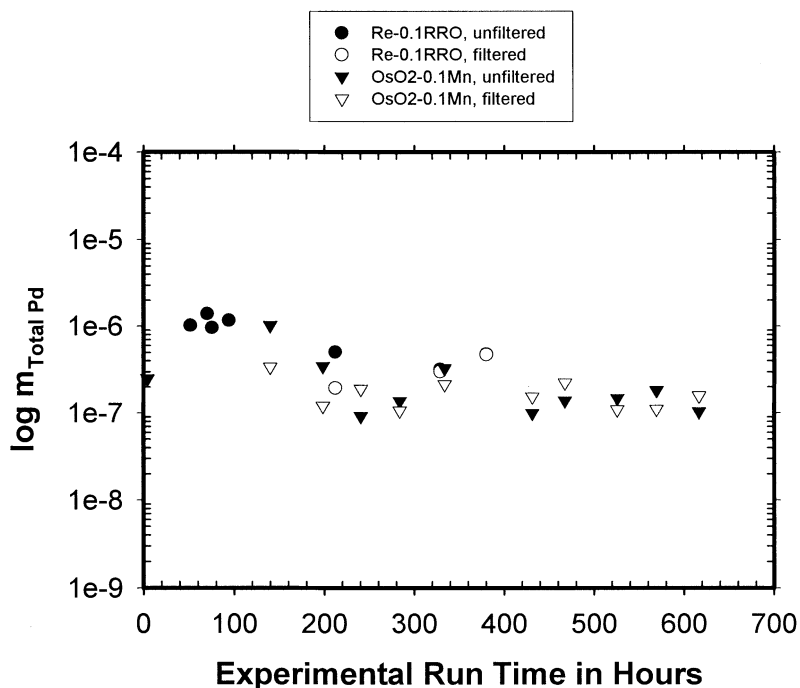


Fig. 3. Palladium concentrations from two experimental runs at 400 °C and 500 °C. Notice that the equilibrium was attained after 400 hour at 400 °C, and after 200 hours at 500 °C

obtained after 450 hours (see discussion below), except a few deviating significantly from the means, were included. Similarly, the average equilibrium concentration of Pd at 400 °C was calculated using all of the data after 400 hours (see discussion below). The average equilibrium concentration of Pd at 500 °C was calculated using all of the data after 200 hours.

The total Os concentrations from the Os-1.0 run in 1.0 m KCl fluid at 500 °C and ~ 800 bars buffered by the K-feldspar-muscovite-quartz assemblage (KMQ) and Ni-NiO (NNO) range from 1 to 23 ppb (4.14×10^{-9} to 1.27×10^{-7} moles/kg H₂O). From the plot of concentration versus run time (Fig. 2), it seems that the experimental run attained equilibrium after 450 hours. The average equilibrium concentration from this experimental run is approximately 3.3 ± 0.5 ppb ($1.93 \pm 0.22 \times 10^{-8}$ moles/kg H₂O). Note that the concentrations of Os in both filtered and unfiltered samples are almost identical (Fig. 2). This is a good indication that osmium is truly in solution.

The osmium concentrations from the Os-1.5 run in 1.5 m KCl fluid at 500 °C and ~ 800 bars also buffered by KMQ and NNO are in the range from 10 to 390 ppb (6.09×10^{-8} to 2.28×10^{-6} moles/kg H₂O) and the average equilibrium concentration is about 126 ± 70 ppb ($6.5 \pm 3.1 \times 10^{-7}$ moles/kg H₂O). In comparison with the Os concentrations in the Os-1.0 run, the values from the Os-1.5 run are considerably higher (Fig. 2). Os-1.0 and Os-1.5 runs are in 1.0 m ($\log a_{\text{Cl}^-} = \sim -1.3$; from EQBRM output) and 1.5 m ($\log a_{\text{Cl}^-} = \sim -1.2$) KCl fluids at 500 °C, respectively. As the pH values in 1.0 m and 1.5 m KCl solutions at 500 °C

Table 2. Experimental results of solubility of osmium and palladium metal under buffered pH and $\log f_{O_2}$ conditions

Experimental run	Experimental conditions	Sample #	Sample mass	Run time (in hours)	Total Os in ppb	Total Os in moles	Total Pd in ppb	Total Pd in moles
Re/Os-1.5	T = 500 °C	Re/Os-1.5-1B	4.368	172	1014	5.93×10^{-6}	N/A	N/A
	P = ~ 800 bars	Re/Os-1.5-2B	4.600	216.2	1184	6.92×10^{-6}	N/A	N/A
	(~ 11500 PSI)	Re/Os-1.5-3B	3.216	264.7	1872	1.09×10^{-5}	N/A	N/A
	pH = ~ KMQ buffer	Re/Os-1.5-4B	2.772	314	2248	1.31×10^{-5}	N/A	N/A
	$\log f_{O_2}$ =	Re/Os-1.5-5B	3.791	359.7	2271	1.33×10^{-5}	N/A	N/A
	RRO buffer	Re/Os-1.5-6B	4.155	409	1796	1.05×10^{-5}	N/A	N/A
	1.5 m KCl	Re/Os-1.5-7B	3.736	456	2007	1.17×10^{-5}	N/A	N/A
		Re/Os-1.5-8B	3.941	505.5	1460	1.44×10^{-5}	N/A	N/A
		Re/Os-1.5-9B	4.637	552	2416	1.41×10^{-5}	N/A	N/A
		Re/Os-1.5-10B	7.805	599.5	1330	7.78×10^{-6}	N/A	N/A
		Re/Os-1.5-11B	4.356	648.5	2289	1.34×10^{-5}	N/A	N/A
		Re/Os-1.5-12B	3.195	696.5	1891	1.11×10^{-5}	N/A	N/A
		Re/Os-1.5-13B	4.137	744.5	1317	7.70×10^{-6}	N/A	N/A
		Re/Os-1.5-14B	3.146	792.8	1337	7.81×10^{-6}	N/A	N/A
		Re/Os-1.5-15B	4.221	840.6	1293	7.56×10^{-6}	N/A	N/A
Os-1.5 Run		Re/Os-1.5-16B	4.193	888.4	1089	6.36×10^{-6}	N/A	N/A
		Re/Os-1.5-17B	3.897	913	1654	9.67×10^{-6}	N/A	N/A
		Re/Os-1.5-18B	4.891	937.2	1007	5.89×10^{-6}	N/A	N/A
	T = 500 °C	Os-1.5-1Bu	1.407	148.5	241	1.41×10^{-6}	N/A	N/A
	P = ~ 800 bars	Os-1.5-1Bf	2.837	same as above	94	5.47×10^{-7}	N/A	N/A
	(~ 11500 PSI)	Os-1.5-2Bu	2.039	196.5	10	6.09×10^{-8}	N/A	N/A
	pH = ~ KMQ buffer	Os-1.5-2Bf	3.242	same as above	59	3.45×10^{-7}	N/A	N/A
	$\log f_{O_2}$ =	Os-1.5-3Bu	2.577	241.7	70	4.09×10^{-7}	N/A	N/A
	NNO buffer	Os-1.5-3Bf	2.846	same as above	250	1.46×10^{-6}	N/A	N/A
		Os-1.5-4Bu	2.817	294	264	1.54×10^{-6}	N/A	N/A

(continued)

Table 2 (continued)

1.5 m KCl	Os-1.5-4Bf	3.348	same as above	60	3.52×10^{-7}	N/A	N/A
	Os-1.5-5Bu	2.900	406.5	59	3.42×10^{-7}	N/A	N/A
	Os-1.5-5Bf	3.316	same as above	42	2.43×10^{-7}	N/A	N/A
	Os-1.5-6Bu	2.023	449.2	215	1.26×10^{-6}	N/A	N/A
	Os-1.5-6Bf	1.787	same as above	368	2.15×10^{-6}	N/A	N/A
	Os-1.5-7Bu	2.142	500	104	6.09×10^{-7}	N/A	N/A
	Os-1.5-7Bf	2.082	same as above	97	5.66×10^{-7}	N/A	N/A
	Os-1.5-8Bu	3.765	544.6	39	2.31×10^{-7}	N/A	N/A
	Os-1.5-8Bf	2.64	same as above	390	2.28×10^{-7}	N/A	N/A
	Os-1.5-9Bu	3.562	594.5	188	1.10×10^{-6}	N/A	N/A
	Os-1.5-9Bf	2.895	same as above	121	7.08×10^{-7}	N/A	N/A
	Os-1.5-10Bu	2.480	714.3	113	6.63×10^{-7}	N/A	N/A
	Os-1.5-10Bf	2.188	same as above	73	4.26×10^{-7}	N/A	N/A
	Os-1.5-11Bu	1.667	759.8	139	8.14×10^{-7}	N/A	N/A
	Os-1.5-11Bf	1.886	same as above	228	1.33×10^{-6}	N/A	N/A
	Os-1.5-12Bu	2.847	810.7	151	8.83×10^{-7}	N/A	N/A
	Os-1.5-12Bf	1.564	same as above	173	1.01×10^{-6}	N/A	N/A
	Os-1.5-13Bu	2.405	861.7	155	9.03×10^{-7}	N/A	N/A
	Os-1.5-13Bf	1.460	same as above	127	7.44×10^{-7}	N/A	N/A
	Os-1.5-14Bu	2.781	908.8	42	2.46×10^{-7}	N/A	N/A
	Os-1.5-14Bf	2.274	same as above	56	3.28×10^{-7}	N/A	N/A
	Os-1.5-15Bu	4.217	975.1	24	1.40×10^{-7}	N/A	N/A
	Os-1.5-15Bf	4.488	same as above	24	1.38×10^{-7}	N/A	N/A
	Os-1.5-16Bu	2.413	1029.9	108	6.30×10^{-7}	N/A	N/A
	Os-1.5-16Bf	1.922	same as above	122	7.10×10^{-7}	N/A	N/A
	Os-1.5-17Bu	2.823	1071.8	150	8.79×10^{-7}	N/A	N/A
	Os-1.5-17Bf	2.653	same as above	94	5.50×10^{-7}	N/A	N/A
	Os-1.5-18Bu	2.948	1118.8	176	1.03×10^{-6}	N/A	N/A
	Os-1.5-18Bf	2.766	same as above	138	8.08×10^{-7}	N/A	N/A

(continued)

Table 2 (continued)

Os-1.0 Run	T = 500 °C	Os-1.0-1Bu	2.972	41.2	1	4.14×10^{-9}	N/A	N/A
	P = ~ 800 bars	Os-1.0-1Bf	5.081	same as above	16	8.80×10^{-8}	N/A	N/A
	(~ 11500 PSI)	Os-1.0-2Bu	4.102	113.5	1	5.37×10^{-9}	N/A	N/A
	pH = ~ KMQ	Os-1.0-2Bf	4.441	same as above	5	2.68×10^{-8}	N/A	N/A
	buffer	Os-1.0-3Bu	3.401	158.7	3	1.52×10^{-8}	N/A	N/A
	$\log f_{O_2} =$	Os-1.0-3Bf	3.322	same as above	3	1.42×10^{-8}	N/A	N/A
	NNO buffer	Os-1.0-4Bu	2.697	211	2	1.23×10^{-8}	N/A	N/A
	1.0 m KCl	Os-1.0-4Bf	2.466	same as above	2	1.24×10^{-8}	N/A	N/A
		Os-1.0-5Bu	3.596	323.5	3	1.66×10^{-8}	N/A	N/A
		Os-1.0-5Bf	3.101	same as above	1	6.46×10^{-9}	N/A	N/A
		Os-1.0-6Bu	3.362	366.2	3	1.58×10^{-8}	N/A	N/A
		Os-1.0-6Bf	3.929	same as above	1	4.65×10^{-9}	N/A	N/A
		Os-1.0-7Bu	3.869	417.3	23	1.27×10^{-7}	N/A	N/A
		Os-1.0-7Bf	3.942	same as above	6	3.56×10^{-8}	N/A	N/A
		Os-1.0-8Bu	4.985	461.6	3	1.95×10^{-8}	N/A	N/A
		Os-1.0-8Bf	4.719	same as above	2	1.34×10^{-8}	N/A	N/A
		Os-1.0-9Bu	3.396	511.5	3	1.80×10^{-8}	N/A	N/A
		Os-1.0-9Bf	3.496	same as above	3	1.69×10^{-8}	N/A	N/A
		Os-1.0-10Bu	4.795	613.3	4	2.49×10^{-8}	N/A	N/A
		Os-1.0-10Bf	lost	same as above	N/A	N/A	N/A	N/A
		Os-1.0-11Bu	6.385	676.8	4	2.23×10^{-8}	N/A	N/A
		Os-1.0-11Bf	5.551	same as above	4	2.07×10^{-8}	N/A	N/A
		Os-1.0-12Bu	6.188	727.7	4	2.04×10^{-8}	N/A	N/A
		Os-1.0-12Bf	5.493	same as above	3	1.87×10^{-8}	N/A	N/A
		Os-1.0-13Bu	4.944	778.7	3	1.94×10^{-8}	N/A	N/A
		Os-1.0-13Bf	4.254	same as above	3	1.75×10^{-8}	N/A	N/A
		Os-1.0-14Bu	6.139	825.8	3	1.89×10^{-8}	N/A	N/A
		Os-1.0-14Bf	5.613	same as above	3	1.89×10^{-8}	N/A	N/A
		Os-1.0-15Bu	6.301	892.1	4	2.08×10^{-8}	N/A	N/A

(continued)

Table 2 (continued)

OsO ₂ -0.1Mn-8Bf	3.858	same as above	22	3.79×10^{-8}	16	1.54×10^{-7}
OsO ₂ -0.1Mn-9Bu	3.414	476.5	14	7.35×10^{-8}	15	1.38×10^{-7}
OsO ₂ -0.1Mn-9Bf	3.744	same as above	7	3.82×10^{-8}	24	2.23×10^{-7}
OsO ₂ -0.1Mn-10Bu	3.985	525.75	11	5.65×10^{-8}	16	1.47×10^{-7}
OsO ₂ -0.1Mn-10Bf	3.704	same as above	13	6.92×10^{-8}	11	1.09×10^{-7}
OsO ₂ -0.1Mn-11Bu	3.837	569.25	5	2.78×10^{-8}	19	1.83×10^{-7}
OsO ₂ -0.1Mn-11Bf	3.867	same as above	17	8.76×10^{-8}	12	1.11×10^{-7}
OsO ₂ -0.1Mn-12Bu	4.493	616.5	19	1.03×10^{-7}	11	1.04×10^{-7}
OsO ₂ -0.1Mn-12Bf	4.674	same as above	< 5?	?	17	1.59×10^{-7}
OsS ₂ -0.1MPP	T = 500 °C*	480	3	1.4×10^{-8}	N/A	N/A
OsS ₂ -0.5MPP	T = 500 °C**	480	27	1.5×10^{-7}	N/A	N/A

Note: All samples in the Re/Os-1.5 Run were unfiltered. In all other runs, each sample was split into two. Unfiltered samples are denoted by 'u', whereas filtered samples are denoted by 'f'. *KMQ* K-feldspar-muscovite-quartz pH buffer; *RRQ* Re-ReO₂ oxygen fugacity buffer; *NNO* Ni-NiO oxygen fugacity buffer; *MMO* MnO-Mn₃O₄ oxygen fugacity buffer. *P = ~550 bars, pH = KMQ buffer, log *f*O₂ and log *f*S₂ = magnetite-pyrite-pyrrhotite buffer, 0.1 m KCl. **P = ~550 bars, pH = KMQ buffer, log *f*O₂ and log *f*S₂ = magnetite-pyrite-pyrrhotite buffer, 0.5 m KCl

Table 3. Average equilibrium concentrations for experiments investigating Os and Pd solubilities

Experimental run number	Average equilibrium concentration of Os (moles/kg H ₂ O) with 2σ	Average equilibrium concentration of Pd (moles/kg H ₂ O) with 2σ
Os-1.0	$1.93 \pm 0.46 \times 10^{-8}$	N/A
Os-1.5	$6.50 \pm 6.20 \times 10^{-7}$	N/A
Re/Os-1.5	$1.05 \pm 0.52 \times 10^{-5}$	N/A
Re-0.1RRO	N/A	$3.8 \pm 2.0 \times 10^{-7}$
OsO ₂ -0.1Mn	$6.9 \pm 5.2 \times 10^{-8}$	$1.42 \pm 0.74 \times 10^{-7}$

are identical (Table 1), the higher Os concentrations in Os-1.5 run than in Os-1.0 run imply the likely presence of an Os chloride complex. The likely existence of a chloride species is also supported by the experiments involving OsS₂ in which OsS₂-0.5 MPP run (0.5 m KCl) has higher Os concentrations (27 ppb; $\sim 1.5 \times 10^{-7}$ moles/kg H₂O) than OsS₂-0.1 MPP run (0.1 m KCl) (3 ppb Os; $\sim 1.4 \times 10^{-8}$ moles/kg H₂O) (Table 2).

In 1.5 m KCl solution in the presence of the higher log f_{O_2} buffer (Re-ReO₂ buffer, RRO) at 500 °C and ~ 800 bars (Re/Os-1.5 run), Os concentrations are even higher (ranging from 1007 to 2416 ppb; 5.89×10^{-6} to 1.41×10^{-5} moles/kg H₂O) and the average equilibrium concentration is 1705 ± 399 ppb ($1.05 \pm 0.26 \times 10^{-5}$ moles/kg H₂O).

In experiments using Pd metal as starting material, equilibrium was attained after 200 hours at 500 °C and after 400 hours at 400 °C (Fig. 3). There is also good agreement between concentrations from filtered and unfiltered samples (Fig. 3), suggesting that Pd is truly in solution. The palladium concentrations from the Re-0.1RRO run in a 0.1 m KCl solution at 500 °C and 550 bars buffered by RRO range from 21 to 147 ppb (1.99×10^{-7} to 1.39×10^{-6} moles/kg H₂O) (Table 2). The average equilibrium concentration of Pd is approximately 40 ± 10 ppb ($3.79 \pm 0.95 \times 10^{-7}$ moles/kg H₂O). The palladium concentrations from the OsO₂-0.1 Mn run (OsO₂ as starting material for Os) in a 0.1 m KCl solution at 400 °C and 550 bars buffered by the assemblage of MnO-Mn₃O₄ are from 10 to 108 ppb (9.46×10^{-8} to 1.02×10^{-6} moles/kg H₂O) (Table 2). The average equilibrium concentration is approximately 15 ± 4 ppb ($1.42 \pm 0.37 \times 10^{-7}$ moles/kg H₂O). Also in the OsO₂-0.1 Mn run, the osmium concentrations range from less than 5 to 65 ppb (2.65×10^{-8} to 3.44×10^{-7} moles/kg H₂O) and the average equilibrium concentration is about 13 ± 5 ppb ($6.88 \pm 2.64 \times 10^{-8}$ moles/kg H₂O). As the f_{O_2} of MnO-Mn₃O₄ buffer at 400 °C is about $10^{-23.5}$ bars (calculated from the equation of Chou, 1987) and that of RRO buffer at 500 °C is about $10^{-20.0}$ bars (calculated from the equation of Pownceby and O'Neil, 1994), the slightly higher concentrations at 500 °C may be mainly due to the effect of oxygen fugacity.

The general solubility reactions in our experiments can be written as follows:



If the equilibrium constant expressions for reactions (9) and (10) are expressed in logarithmic form and rearranged, when temperature, pressure, activities of chloride and hydrogen are constant, in $\log \Sigma\text{Os}$ or $\log \Sigma\text{Pd}$ versus $\log f_{\text{O}_2}$ space, the oxidation state(s) of Os or Pd can be evaluated according to the slope m or x :

$$(\partial \log \Sigma\text{Os} / \partial \log f_{\text{O}_2})_{T,P,a_{\text{Cl}^-},p\text{H}} = m$$

$$(\partial \log \Sigma\text{Pd} / \partial \log f_{\text{O}_2})_{T,P,a_{\text{Cl}^-},p\text{H}} = x$$

As our experiments on Os solubility were conducted using two different oxygen fugacity buffers (RRO in Re/Os-1.5 run and NNO in Os-1.5 run) in which other experimental parameters are the same (Table 2), the oxidation state of aqueous Os can be tentatively assessed. As the slope is approximately $0.42 \pm \begin{smallmatrix} 0.14 \\ 0.10 \end{smallmatrix}$ (the positive error is calculated assuming that only positive errors are associated with the average concentrations, whereas the negative error was calculated assuming that only negative errors are associated with the average concentrations), the dominant oxidation state of Os can be tentatively determined to be +2 (for which the slope would be 0.50). However, there could be a small contribution from Os^{1+} or Os^{3+} or higher valence state. It is of interest to note that *Sassani and Shock* (1998) have predicted that the stable oxidation states of Ru and Rh in most hydrothermal environments would be Rh^{2+} and Ru^{2+} . As we already know that Pd^{2+} and Pt^{2+} are the predominant states for these metals (cf. *Mountain and Wood*, 1988), an oxidation state of Os^{2+} would thus be consistent with the other PGE. The likelihood of an Os^{2+} oxidation state is also supported by the fact that Os^{1+} is stable only in the presence of ligands of the so-called “back-bonding” type such as carbon monoxide (*Livingstone*, 1973; *Westland*, 1981). However, further experiments are needed to confirm this conclusion. Assuming an oxidation state of +2, therefore, the solubility reaction involving Os can be written as:



where n can only be firmly established by further experiments.

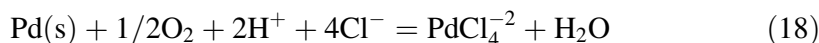
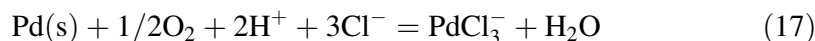
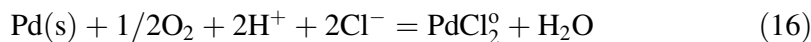
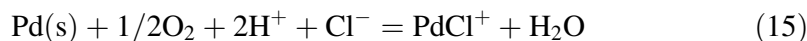
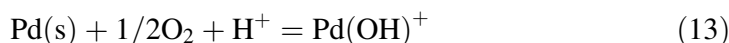
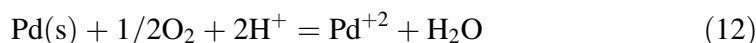
Implications

Based on our experimental results, the following conclusions can be reached: (1) Metallic osmium and palladium are soluble in detectable amounts in saline, high-temperature, sulfur-free, slightly acidic, and relatively oxidizing fluids; (2) the solubilities of Os and Pd show a dependence on chloride concentration, suggesting the likely presence of chloride species. Although strictly speaking these conclusions are limited to the experimental parameters used in our experiments, they have potential bearing on PGE mineralization processes under similar or more severe conditions. Porphyry systems represent one such environment. In the following, our discussions focus on the comparison of experimental data with theoretical calculations followed by applications to porphyry systems.

It should be emphasized that, although there have been theoretical calculations on the solubility of PGE (excluding Os and Ir) under supercritical conditions (*Sassani and Shock*, 1990, 1998), it will become clear below that such calculations conflict with both field observations and experimental work and therefore their reliability is questionable.

Direct evaluation of theoretical calculations in the context of porphyry environments

Our results on the solubility of Pd metal in combination with the following field observations provide an excellent opportunity to evaluate theoretical calculations on the solubility of PGE (*Sassani and Shock, 1990, 1998*) under supercritical conditions relevant to porphyry environments. As *Sassani and Shock (1998)* considered that their recent data base supersedes that of 1990, that data base is used here. To evaluate their calculations, parameters for HKF equations for palladium chloride and sulfate complexes are employed to modify the data base of SUPCRT92 (*Johnson et al., 1992*). Two Pd solid phases, metallic palladium and vysotskite (PdS), for which *Sassani and Shock (1998)* provide data, are adopted for the evaluation as the former may be assumed to be representative of sulfur-poor environments and the latter is representative of sulfur-rich environments. Their calculations are first directly compared with our experimental results in sulfur-free, KCl fluids. For such sulfur-free, chloride-containing environments, the following equations were considered:



Equilibrium constants for reactions (12) through (18) were calculated from SUPCRT92 using the modified data base. ΣPd is the sum of $[\text{PdO}^0]$, $[\text{Pd}^{+2}]$, $[\text{Pd(OH)}^+]$ and $[\text{PdCl}_n^{2-n}]$. From Table 4, it is clear that theoretical calculations of *Sassani and Shock (1998)* underestimate the measured solubilities of Pd at 400 °C and 500 °C by at least six and four orders of magnitude, respectively. As the parameters in Table 4 are relevant to porphyry systems, the underestimation of solubilities of Pd by many orders of magnitude by models of *Sassani and Shock (1998)* suggests that deficiencies in such models need to be redressed in order to place constraints on the geochemical behavior of PGE in such environments in concordance with experimental studies and field observations (see below). In the following, field observations are further compared with both our experimental results and theoretical calculations of *Sassani and Shock (1998)* to assess their respective applicability into porphyry systems.

Applications to porphyry systems

In porphyry systems, temperature of ore formation typically ranges from 350° to 550 °C (*Beane and Titley, 1981; Beane, 1982; Eliopoulos and Economou-Eliopoulos, 1991; Tarkian and Koopmann, 1995*). Moderately acidic to highly acidic pH is indicated by the presence of alteration assemblages such as, in order of

Table 4. Comparison of Pd solubility in sulfur-free environments at 400 °C and 500 °C

Sources	Temperature	Solid phase	$\log f_{\text{O}_2}$	pH	$\log a_{\text{Cl}^-}$	Σ Pd in moles/kg H ₂ O	Σ Pd in ppb
Sassani and Shock (1998)	400 °C	Pd Metal	- 23.46	5.0	- 1.5	$10^{-13.5}$	$\sim 3 \times 10^{-6}$
this study	500 °C	Pd Metal	- 20.02	5.5	- 2.6	$10^{-11.1}$	$\sim 9 \times 10^{-4}$
	400 °C	Pd Metal	- 23.46, MnO-Mn ₃ O ₄ buffer	~ 5.0 , KMQ buffer	- 1.5	$10^{-6.85}$	~ 15
	500 °C	Pd Metal	- 20.02, RRO buffer	~ 5.5 , KMQ buffer	- 2.6	$10^{-6.42}$	~ 40

decreasing pH, the potassic assemblage (K-feldspar + muscovite (sericite) + biotite + quartz), the phyllic assemblage (quartz + sericite + pyrite) and the argillic assemblage (kaolinite + montmorillonite + chlorite) (*Beane*, 1982). A relatively high oxygen fugacity is indicated by the common occurrence of both magnetite and hematite in the potassic alteration zone, which suggests that oxygen fugacity is probably close to values defined by the magnetite-hematite buffer (*Beane*, 1982). The salinity of the ore-forming fluids is typically up to 30 to 60 wt.% eq. NaCl (~ 7.3 moles/kg H₂O to ~ 25.6 moles/kg H₂O) (*Beane and Titley*, 1981). Most of these physicochemical parameters are comparable to our experimental conditions, but salinity is far higher than in our experiments. Therefore, in the earlier stages of porphyry systems, fluids are fully capable of transporting at least 10 ppb Pd and Os (Table 2) if the solubility-controlling phases are metallic Pd and Os and sources for PGE are available. Existing field observations can be used to test this prediction. It should be stressed that the solubility-controlling phase for Pd and Os in porphyry systems presently is not well known. As for Pd, metallic Pd and vysotskite are the stable phase in reduced sulfur-deficient and reduced sulfur-rich environments, respectively (*Mountain and Wood*, 1988; *Sassani and Shock*, 1998). In porphyry systems, it has been observed that anhydrite (CaSO₄) is predominantly early (*Crerar and Barnes*, 1976) and occurs in the potassic zone (*Beane*, 1982). Therefore, in the formation process of porphyry systems, especially in the early stage, there are periods when oxidized sulfur species are important. During such periods, metallic Pd may control the solubility.

In the Skouries porphyry deposit, Greece, the average contents of Pd and Ru are about 180 ppb and 26 ppb, respectively (*Eliopoulos and Economou-Eliopoulos*, 1991). As the ore reserves amount to 72 million tons (*Frei*, 1995), the amounts of Pd and Ru in the Skouries deposit are approximately 13 tons and 2 tons, respectively. *Tarkian and Koopmann* (1995) reported that mineralized quartz diorites in the Santo Tomas II (Philex) porphyry copper deposits carry an average of ~ 50 ppb for Pd and of ~ 15 ppb for Pt. The reserve tonnage of ores at the Philex deposit is $\sim 60 \times 10^6$ short tons (*Gilmour*, 1982) ($\sim 5 \times 10^{13}$ grams). Consequently, the total Pd in the Philex deposit can be roughly approximated to be 2.5 tons. In the Robinson district, White Pine County in Nevada, stockwork porphyry copper deposits have Pd and Pt grades of 10 ppb and 3 ppb, respectively (*Smith*, 1976; *Bonham*, 1989). The total mined tonnage of ores in the Robinson district is estimated to be about 253 million tons ($\sim 2.5 \times 10^{14}$ grams) (*Smith*, 1976) and the total tonnage of ore reserves is estimated to be 537 million tons ($\sim 5.4 \times 10^{14}$ grams) (*James*, 1976; *Laznicka*, 1985). There are six major porphyry copper deposits in this district (*Smith*, 1976). Therefore, the maximum tonnage of Pd is approximately 5.4 tons and the average tonnage of Pd for each porphyry deposit is approximately 1 ton. Applying our experimental data, we can calculate the total amount of Pd that can be transported by a typical porphyry system. *Sutulov* (1974) suggested that the average tonnage for copper in a typical porphyry system is about 1 million tons (10^{12} grams). *Crerar and Barnes* (1976) argued that copper concentrations in a porphyry-forming fluid are at the 1000 ppm level. Therefore, the total amount of fluid in a typical porphyry system is in the neighborhood of 10^{15} grams. Considering the equilibrium concentration of Pd at 500 °C (~ 40 ppb, RRO buffer) or at 400 °C (~ 15 ppb, MnO-Mn₃O₄ buffer) from

our experiments and assuming that the solubility-controlling phase is metallic Pd, we estimate that the total Pd transported by a porphyry system can be as high as ~ 40 tons or 15 tons. When taking into account the uncertainties in estimation, our experimental results are in good agreement with field observations. Therefore, it appears that porphyry systems are capable to transport significant amounts of Pd as chloride complexes if the sources for PGE are available and the fluids are sulfur-poor. Notice that for PGE mineralization, deposits with a tonnage at the 10^2 level are considered to be large deposits (*Laznicka, 1999*). Consequently, it can be suggested conservatively that porphyry systems have the capacity to form at least mid-sized PGE deposits.

We also can estimate conservatively how much osmium can be transported by the aforementioned model porphyry system using the solubility data for a 1.0 m KCl solution buffered by NNO at 500 °C (~ 3 ppb). Employing the total fluid mass of 10^{15} grams in the model porphyry system, the amount of osmium that can be transported is calculated to be ~ 3 tons. In the Chenmenshan porphyry deposit in Juijiang, Jiangxi Province, China, the grade of osmium was determined to be 1 ppb to 2.4 ppb (*Chang et al., 1991, p. 279*). It should be pointed out that the grade seems low, but these Os contents are about two orders of magnitude higher than those of unmineralized felsic rocks in comparison with the average concentration of analogous Ir for felsic rocks (0.006 ppb) (*Crocket, 1981*). The use of Ir concentrations for felsic rocks to approximate those of Os is required because reliable Os data for felsic rocks are not available and to a first approximation, $Os \cong Ir$ (*Crocket, 1981*). The reserves of Cu in this deposits were 2.1×10^6 tons (*Zhai et al., 1996, p. 238*) and the grade of Cu was 0.75% (*Chang et al., 1991, p. 239*). Therefore, the total amount of ore is estimated to be $\sim 2.8 \times 10^{14}$ grams. Hence the amount of Os that had been transported is computed to be 0.24 tons. This value is below the maximum capacity of the above-mentioned model porphyry system, suggesting that the ore-forming fluid may have been undersaturated with Os, probably because of the lack of source materials assuming that metallic Os was the solubility-controlling phase. Undersaturation is also supported by the data on Pd. The grade of Pd in this deposit is 1 ppb (*Chang et al., 1991, p. 279*). Using the above reserves of ores, the total amount of Pd that had been transported is calculated to be 0.1 tons. This value is one to two orders of magnitude smaller than those in the Skouries deposit, Philex deposit and in the Robinson district, implying that the ore-forming fluid was also undersaturated with respect to Pd if the solubility-controlling phase was metallic Pd and all transported PGE had been deposited. However, solubilities of Pd and Os sulfides and other phases (such as alloys; *Gammons et al., 1993*) could be orders of magnitude lower. So another possibility is that Pd and Os metals may not be the solubility-controlling phases in this deposit.

From the above calculations, an important conclusion can be drawn: porphyry systems have considerable capacity for the transport of PGE if source materials are available. A logical inference is that there is potential for finding PGE deposits hosted by porphyry systems when such systems are associated with PGE-enriched rocks (such as mafic to ultramafic rocks, black shales, etc.). For instance, the above-mentioned Robinson district in White Pine County, Nevada, is adjacent to Eureka County where black shales have been observed to contain high

Table 5. Comparison of field observed PGE transported by typical porphyry systems with those predicted by Sassani and Shock (1998) and predicted by this study[#]

Predictions or field observations	Temperature	Solubility controlling phase	$\log f_{\text{O}_2}$	pH	$\log a_{\text{Cl}^-}$	$\log a_{\Sigma\text{S}}$	Transportable PGE assuming saturation with solid phase (in grams)
Sassani and Shock (1998)	400 °C	Pd Metal	-23.46	5.0	-1.5	N/A	~ 10 (Pd)
		PdS	-23.46	5.0	-1.5	-1.0	$\sim 10^{-5}$ (Pd)
		Ru Metal	-23.46	5.0	-1.5	N/A	$\sim 10^{-3}$ (Ru)
		RuS ₂	-23.46	5.0	-1.5	-1.0	$\sim 10^{-14}$ (Ru)
	500 °C	Pd Metal	-20.02	5.5	-2.6	N/A	$\sim 10^3$ (Pd)
		PdS	-20.02	5.5	-2.6	-1.0	$\sim 10^{-5}$ (Pd)
		Ru Metal	-20.02	5.5	-2.6	N/A	$\sim 10^{-1}$ (Ru)
		RuS ₂	-20.02	5.5	-2.6	-1.0	$\sim 10^{-18}$ (Ru)
This study	400 °C	Pd Metal	-23.46, MnO-Mn ₃ O ₄ buffer	~ 5.0 , KMQ buffer	~ -1.5	N/A	$\sim 1.5 \times 10^7$ (Pd)
		Pd Metal	-20.02, RRO buffer	~ 5.5 , KMQ buffer	~ -2.6	N/A	$\sim 4 \times 10^7$ (Pd)
	500 °C	Os Metal	-22.88, NNO buffer	~ 4.6 , KMQ buffer	~ -1.3	N/A	$\sim 3 \times 10^6$ (Os)
Field observations	350 ° to 550 °C	Unknown	Magnetite-hematite buffer*	KMQ buffer	-1.0**	-1***	$\sim 1 \times 10^6$ to 1.3×10^7 (Pd) $\sim 2 \times 10^6$ (Ru)

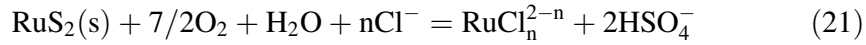
[#]In calculations of PGE transported by a typical porphyry system predicted by this study and Sassani and Shock (1998), the total mass of fluids in the system is assumed to be 10^{15} grams (see text for details). * Notice that the oxygen fugacity provided by MnO-Mn₃O₄ buffer is close to that of magnetite-hematite buffer in the temperature range from 350° to 550 °C (see Fig. 1). ** According to Creer and Barnes (1976). *** $\log m_{\Sigma\text{S}}$; from Creer and Barnes (1976)

concentrations of PGE (Pd, 10 to 13 ppb; Pt, up to 30 ppb) (*Pařava*, 1993). This would have an important bearing on exploration. The above calculations also imply that the lack of Os mineralization in known porphyry deposits may be due to the paucity of source materials for this metal.

In Table 5, the amounts of PGE that can be transported by a typical porphyry system as predicted by this study and that using the model of *Sassani* and *Shock* (1998) are summarized in comparison with field observations. Notice that, if Os is used as a proxy for Ru because of their geochemical similarity (Ir group) (*Crocket*, 1981; *Barnes* et al., 1985), our conservative estimation of transportable Os (~3 tons) also agrees with field observed Ru tonnage (~2 tons). To apply the theoretical calculations of *Sassani* and *Shock* (1998) to estimate the maximum amounts of Pd and Ru that can be transported, there are two types of environments to be considered: (1) sulfur-free or sulfur-poor and (2) sulfur-rich environments. For sulfur-free or sulfur-poor environments, reactions (12) through (18) and similar reactions for ruthenium metal (to save space, they are omitted) prevail. For sulfur-rich environments, the following two general reactions for vysotskite are taken into account:



where $n = 1, 2, 3$ and 4 , and $m = 1, 2$ and 3 . Hence, ΣPd is the sum of $[\text{PdCl}_n^{2-n}]$ and $[\text{Pd(SO}_4)_m^{2-2m}]$. Similarly, for sulfur-rich environments, the following two general reactions are considered for laurite:



Quantitatively, it is obvious from Table 5 that the theoretical calculations of *Sassani* and *Shock* (1998) underestimate the amount of palladium that can be transported by a typical porphyry system by at least four orders of magnitude in comparison with field observations and our experimental data. They also underestimate the amount of ruthenium transported by porphyry systems by at least seven orders of magnitude in comparison with field observations. Qualitatively, such theoretical calculations simply fail to predict the existence of PGE mineralization associated with porphyry systems. Therefore, it can be concluded that the theoretical calculations of *Sassani* and *Shock* (1998) on palladium and ruthenium at elevated temperatures need to be refined.

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Authors' address: Dr. *Y. Xiong* and Prof. *S. A. Wood*, Laboratory for Experimental Aqueous Geochemistry, Department of Geology and Geological Engineering, University of Idaho, Moscow, ID 83844-3022, U.S.A., e-mail: xiong932@uidaho.edu; swood@uidaho.edu