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Geochimica et Cosmochimica Acta

Geochimica et Cosmochimica Acta 73 (2009) 438-454

www.elsevier.com/locate/gca

Platinum solubility and partitioning in a felsic melt-vapor-brine assemblage

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Received 4 June 2008: accepted in revised form 20 October 2008: available online 29 October 2008

Abstract

The solubility and partitioning of Pt in a S-free vapor - brine - rhyolite melt - Pt metal assemblage has been quantified at 800 °C, f_{O_2} = NNO and pressures of 100 and 140 MPa. Vapor and brine were sampled at run conditions by trapping these phases as glass-hosted fluid inclusions as the melt cooled through the glass transition temperature. The vapor and brine were in equilibrium with the melt at the time of trapping and, thus, represent fluids which were sampled at the termination of each experimental run. The microthermometrically determined salinities of vapor and brine are ~ 2 and ~ 63 wt.% NaCl eq. and ~ 9 and ~43 wt.% NaCl eq. at 100 and 140 MPa, respectively. Platinum solubilities in vapor, brine and glass (i.e., quenched melt) were quantified by using laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS). Equilibrium is discussed with reference to the major and trace element concentrations of glass-hosted fluid inclusions as well as the silicate melt over run times that varied from 110 to 377 h at 140 MPa and 159 to 564 h at 100 MPa. Platinum solubility values $(\pm 1\sigma)$ in H_2O -saturated felsic melt are $0.28 \pm 0.13 \mu g/g$ and $0.38 \pm 0.06 \mu g/g$ at 140 and 100 MPa, respectively. Platinum solubility values $(\pm 1\sigma_x)$ at 140 and 100 MPa, respectively, in aqueous vapor are $0.91 \pm 0.29 \ \mu g/g$ and $0.37 \pm 0.17 \ \mu g/g$ and in are brine $16 \pm 10 \,\mu\text{g/g}$ and $3.3 \pm 1.0 \,\mu\text{g/g}$. The measured solubility data were used to calculate Nernst-type partition coefficients for Pt between vapor/melt, brine/melt and vapor/brine. The partition coefficient values $(\pm 1\sigma_{\bar{x}})$ for vapor/melt, brine/melt and vapor/brine at 140 MPa are 2.9 ± 1.0 , 67 ± 27 , and 0.13 ± 0.05 and at 100 MPa are 1.0 ± 0.2 , 6.8 ± 2.4 , and 0.15 ± 0.05 . The partitioning data were used to model the Pt-scavenging capacity of vapor and brine during the crystallization-driven degassing (i.e., second boiling) of a felsic silicate melt over a depth range (i.e., 3–6 km) consistent with the evolution of magmatic-hydrothermal ore deposits. Model calculations suggest that aqueous vapor and brine can scavenge sufficient quantities of Pt, and by analogy other platinum group elements (PGE), to produce economically important PGE-rich magmatic-hydrothermal ore deposits in Earth's upper continental crust.

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1. INTRODUCTION

Numerous studies have elucidated the physical and chemical genetic link between shallow-level magma bodies and stratigraphically higher porphyry ore deposits (Emmons, 1927; Sillitoe, 1979, 1989, 1993a, b, 2000; Burnham, 1979; Titley, 1981; Singer and Cox, 1986; Dilles, 1987; Richards et al., 1991; Vila and Sillitoe, 1991; Heinrich et al., 1992,

1999; Vennemann et al., 1993; Hedenquist and Lowenstern, 1994; Shinohara and Kazahaya, 1995; Thompson et al., 1995; Shinohara and Hedenquist, 1997; Audétat et al., 1998, 2000; Hedenquist et al., 1998; Pettke et al., 2001; Muntean and Einaudi, 2001; Ulrich et al., 2001; Halter et al., 2002, 2005; Redmond et al., 2004; Rusk et al., 2008). The chemical characterization of fluid and melt inclusions, using techniques such as laser ablation-inductively coupled-plasma mass spectrometry (LA-ICP-MS), from shallow-level magmatic intrusions, some associated directly with overlying porphyry deposits, indicates that the mass transfer of metals from magma to the porphyry environment occurs

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^{0016-7037/\$ -} see front matter © 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.gca.2008.10.020

via the evolution of a magmatic fluid that can be highly effective at scavenging and transporting ore metals from the silicate melt phase into the overlying porphyry environment where metal precipitation occurs owing to changes in fluid pressure, temperature and chemistry (cf. Redmond et al., 2004; Zajacz and Halter, 2007; Rusk et al., 2008; Zajacz et al., 2008). Experimental studies have constrained the solubilities of ore metals (i.e., As, Au, Cu, Ag and Mo) in magmatic volatile phases in equilibrium with silicate melts (Candela and Holland, 1984; Williams et al., 1995; Frank et al., 2002; Simon et al., 2005, 2006, 2007b, 2008; Keller, 2008) and these data have been used to model quantitatively the behavior of metals at conditions relevant to shallow-level magma degassing. One important group of ore metals for which there are only very limited solubility data at magmatic conditions is the platinum group elements (PGE). Several experimental studies have been performed to characterize the behavior of the PGE in low-temperature fluids; however, the mobility of the PGE in fluid-saturated silicate melt assemblages remains almost completely unconstrained. Acquiring these data is important not only for improving our understanding of PGE-mobility in aqueous-fluid-saturated mafic intrusive bodies (e.g., Stillwater, Bushveld), where aqueous fluids have been postulated to be important PGE-transporting agents (Boudreau et al., 1986; Boudreau and McCallum, 1989, 1992; Meurer and Boudreau, 1996; Meurer et al., 1998; Boudreau and Meurer, 1999), but also in porphyry deposits owing to the interest in constraining their PGE-potential (cf. Economou-Eliopoulos. 2005).

Experiments to constrain PGE mobility in aqueous fluids at temperatures up to 300 °C demonstrate that Pt and Pd are soluble with HS⁻ and Cl⁻ ligands and that PGE solubilities are maximized in highly-saline, acidic aqueous fluids at highly oxidized (i.e., in the hematite stability field) conditions (Gammons et al., 1992; Wood, 2002). Platinum and Pd are soluble as $PtCl_3^-$ and $PdCl_4^{2-}$ in NaCl-H₂O vapor (0.01-3.0 molal NaCl) at 300 °C and saturated water vapor pressure (SWVP) with total Pt and Pd concentrations of ≥ 1 ng/g each in the fluid phase (Gammons et al., 1992). Platinum and Pd are soluble as $Pt(HS)_2$ and $Pd(HS)_2$ in H₂S-rich aqueous solutions over a temperature range of 30 to 300 °C with metal solubilities <0.1 ng/g (Gammons and Bloom, 1993). This latter study found that metal-chloride solubilities are much lower if H₂S dominates the aqueous solution. These data demonstrate that Pt and Pd can be transported as both Cl- and S-complexes in natural systems. Theoretical modeling of PGE mobility using these low temperature data has resulted in inconsistent estimates of PGE solubility at magmatic conditions (Sassani and Shock, 1990, 1998; Wood, 2002). Xiong and Wood (2000) determined experimentally that Pd solubility in 0.01 m KCl supercritical aqueous fluid is 40 ng/g at 400 °C and 15 ng/g at 500 °C. These experimental solubility values are six and four orders of magnitude higher at 400 °C and 500 °C, respectively, than theoretical values calculated by Sassani and Shock (1990, 1998). The large inconsistency demonstrates that extrapolating room temperature solubility data to high temperatures may result in underestimation of actual solubility values; hence, accurate models of PGE mobility in magmatic-hydrothermal fluids require careful experimental work at high temperature.

A limited number of studies have been performed to elucidate PGE solubilities in aqueous fluids at elevated temperatures. Fleet and Wu (1993, 1995) found that the coexistence of Cl and S enhances the volatility of the PGE in anhydrous experiments at 1000 °C and SVP. Such a synergistic effect of volatile Cl and S to enhance metal volatility in hydrous systems at high temperature has been reported recently for Fe and Cu at magmatic conditions (Simon et al., 2002, 2005, 2006). Ballhaus et al. (1994) studied Pt solubility at 900 °C and 1 GPa by trapping supercritical fluids as synthetic fluid inclusions in pre-fractured quartz cores. Their data, however, are difficult to interpret owing to the order-of-magnitude variation in Pt concentrations in the fluid inclusion populations; Pt concentrations range from below detection to several weight percent in fluids recovered from single experiments. Ballhaus et al. (1994) hypothesize that the accidental trapping of Pt nuggets into some fluid inclusions during inclusion formation is responsible for the extreme Pt concentration variability.

Hanley et al. (2005) quantified the Pt concentrations of synthetic aqueous brines at 600 and 800 °C, at a pressure of 150 MPa, by trapping brine as synthetic fluid inclusions in pre-fractured quartz. They report Pt concentrations of up to $1000 \,\mu\text{g/g}$ in hypersaline fluid; however, the experiments suffer in similar fashion as those of Ballhaus et al. (1994) in that Pt concentrations vary by up to three orders of magnitude in single experiments. Hanley et al. (2005) report platinum concentrations that range from 330 to 4556 µg/g at 800 °C, 150 MPa and brine salinity of 70 wt.% NaCl eq. and from 4 to $469 \,\mu\text{g/g}$ at 800 °C, 150 MPa and brine salinity of 50 wt.% NaCl eq. Hanley et al. (2005) suggest that the maximum Pt concentrations in late, primary fluid inclusions from a given experiment yield reasonable estimates of Pt solubility, based on arguments that relate healing of inclusions in quartz fractures to the time necessary for the brine to reach Pt saturation. However, the reported Pt solubilities are orders of magnitude higher than those predicted by theoretical studies (Sassani and Shock, 1998). The Pt concentrations in brine and co-existing silicate melt, the product of melting the pH buffer assemblage albite-andalusite-quartz which yields a melt composition of Ab₅₀Qz₄₁Or₅Co₅, reported in Hanley et al. (2005) yield partition coefficient values for Pt between brine and silicate melt, $D_{\rm Pt}^{brine/melt}$, that range from 6.6×10^3 to 5.2×10^4 at 20 wt.% NaCl eq. and 1.0×10^2 to 2.6×10^4 at 70 wt.% NaCl eq. The high Pt concentrations for the brine may be the product of the use of extremely peraluminous silicate melts (aluminum saturation index ranges from 1.33 to 1.49) which can buffer the HCl concentration of the aqueous brine to very high values (Williams et al., 1997) and may result in anomalously high Pt concentrations relative to lower-HCl conditions expected in natural magmatichydrothermal aqueous fluids. Hence, such conditions may not be representative of those encountered in most magmatic-hydrothermal porphyry environments. The measured Pt concentrations and calculated partition coefficient values suggest that Pt may be highly soluble in hypersaline magmatichydrothermal aqueous fluid, but the clear disequilibrium nature of the run products do not allow the data to be of significant use in modeling efforts.

To circumvent the possible problems induced by using quartz-hosted synthetic fluid inclusions, Hanley and Heinrich (2007) performed experiments wherein hydrous salt melt (75 wt.% $CaCl_2 + MgCl_2$, 25 wt.% H_2O) was equilibrated with tremolite-diopside-enstatite-quartz, an assemblage used to buffer HCl, and either Pt or sperrylite (PtAs₂). They quantified the solubility of Pt in the salt melt by trapping salt melt in both a granular quartz trap and also in pre-fractured quartz cores (3 mm by 10 mm) and analyzing the salt melt in each trapping medium by using LA-ICP-MS. The solubility of Pt in the salt melt, equilibrated with Pt metal, trapped in healed quartz fractures ranges from below detection ($\sim 0.1 \,\mu g/g$) to 14.4 $\mu g/g$ with 28 LA-ICP-MS analyses performed. The solubility of Pt in the salt melt, equilibrated with sperrylite, trapped in healed quartz fractures ranges from below detection $(\sim 0.1 \,\mu\text{g/g})$ to 6.6 $\mu\text{g/g}$ with 28 LA-ICP-MS analyses performed. The solubility of Pt in the salt melt, equilibrated with Pt metal, trapped in the granular quartz medium is $14.4 \pm 6.7 \,\mu\text{g/g}$ with 6 LA-ICP-MS analyses performed. The solubility of Pt in the salt melt, equilibrated with sperrylite, trapped in the granular quartz medium is $4.6 \pm 1.9 \,\mu\text{g/g}$ with 6 LA-ICP-MS analyses performed. The results of their study indicate that Pt is highly soluble in hydrous salt melts and that these types of melts may be quite efficient at mobilizing Pt, and other PGE, in magmatic systems. Importantly, these data indicate that the high Pt solubilities reported in Hanley et al. (2005) likely overestimate by several orders of magnitude the solubility of Pt in magmatic brines at reasonable HCl concentrations. Hanley and Heinrich (2007) suggest, based on their measurements of Pt solubility in quartz-hosted fluid inclusions, that using pre-fractured quartz cores to trap fluid inclusions may result in premature trapping of unequilibrated brine as they observed in Hanley et al. (2005).

Extant data indicate that the solubility of the PGE can be quite high in aqueous fluids over a wide range of conditions, extending from low-temperature epithermal environments to high-temperature magmatic conditions, although the data at the upper temperature conditions attending magma degassing are quite limited and there are no data that constrain the solubility of Pt in low-density, magmatic aqueous fluids. The solubility data for Pt in high-density aqueous-salt fluids are appropriate only for highly saline fluids which may be less important for metal scavenging in causative magmas beneath porphyry environments where the first-exsolved aqueous fluids typically have salinities on the order of 2-10 wt.% NaCl eq. (cf. Williams-Jones and Heinrich, 2005). There are porphyry systems wherein the causative magma evolved brines in the absence of low-salinity fluids (cf. Cline and Bodnar, 1994), but these appear to be the exception rather than the rule. In the current study, we report data that constrain the solubility of Pt in rhyolite melt, low-density vapor and high-density brine at 800 °C and pressures of 100 and 140 MPa. These conditions fall within the depth and temperature range over which magmatic-hydrothermal fluids evolve to produce porphyry-ore deposits. The data constrain the relative Pt-carrying capacity of both low- and high-density aqueous fluids and suggest that felsic magmatic systems may supply significant quantities of Pt, and by analogy other PGE, to porphyryore systems.

2. PROCEDURES

2.1. Starting materials

A synthetic rhyolite melt, $Qz_{0.38}Ab_{0.33}$ Or_{0.29}, was used as the starting melt for all experiments. The composition of the starting glass in wt.% oxides is: SiO₂ = 75.18, Al₂O₃ = 11.09, K₂O = 4.43, Na₂O = 3.67, CaO = 0.17, FeO = 0.35, MnO = 0.01, MgO = 0.10, TiO₂ = 0.03, P₂O₅ = 0.03. The loss on ignition was 4.51%. Aqueous solutions were prepared with reagent grade NaCl and KCl and aqueous HCl. Platinum was added as elemental Pt via the use of Pt capsules. The experiments at 140 MPa also contained Ag and AgCl, added as a 1:1 mixture of Ag:AgCl, to buffer HCl, as discussed below.

2.2. Experiments

Platinum capsules (4.8 mm ID, 5 mm OD, 30 mm length) were loaded with ~ 40 mg rhyolite and 100 µg aqueous solution, sealed and placed in a drying oven (120 °C) for 4 h. Maintenance of capsule mass (± 0.3 mg) over this heating stage was used to verify the mechanical integrity of welded capsules. Capsules were placed inside René-41 cold-seal pressure vessels and pressurized to 50 MPa at ambient temperature. Water was used as the pressure medium, imposed by a Haskell air-driven water-pressure intensifier, and pressure was monitored by using a Bourdon-tube gauge (±2 MPa) calibrated against a factory-calibrated Heise gauge. The vessels were then heated to 800 °C with the pressure line left open to a pressure reservoir buffer. During heating the pressure increases to ~ 100 MPa. Once at 800 °C, pressure was raised to the final desired run pressure. Temperatures were measured with type K (Chromel-Alumel) external thermocouples. The use of René-41 cold-seal pressure vessels (~53 wt.% Ni) imposes an intrinsic oxygen fugacity f_{O_2} that is approximately the value of the nickel-nickel oxide (NNO) buffer (Chou, 1987a). To further constrain the f_{O_2} of each experiment, we loaded a buffer capsule containing elemental Ni and NiO directly behind the experimental charge (at the cold end of the charge) inside the pressure vessel. Following each run the presence of both elemental Ni and NiO were noted in each buffer capsule. The f_{O_2} of the vessels does vary with age owing to continued reaction of the pressure reservoir and the vessel metal. To minimize variation of the intrinsic vessel f_{O_2} over the course of the experimental study, we mechanically abraded the interior of the vessel following each run by using a gun barrel brush to remove scaling and expose a clean vessel surface. The presence of both Ni and NiO in the buffer capsule after each run serves as evidence that each run was at an $f_{O_2} \approx$ NNO. Vessels were placed in tube furnaces and the furnace was tilted such that the hot end of each vessel was oriented in the furnace at a positive 10° angle from the horizontal lab bench to minimize the tempera-

ture gradient (Charles and Vidale, 1982). The temperature gradient in all experimental capsules is $\leq 1.7 \text{ °C cm}^{-1}$ which implies a maximum temperature variation over the diameter of the melt. $\sim 2 \text{ mm}$ at run conditions. of $\sim 0.4 \text{ }^{\circ}\text{C}$: the diameter of the melt is estimated based on the diameter of the recovered glass bead. Experiments were quenched isobarically from 800 to 200 °C by using a stream of compressed air followed immediately by immersion in a room-temperature water bath. Capsules were removed from the vessels, cleaned with lab-grade H₂O and ethyl alcohol, examined optically and weighed to determine if the capsules remained sealed during the experiment. Only capsules that exhibited mechanical integrity, evinced by a mass change ≤ 0.3 mg, and yielded a strong hiss when pierced with a hypodermic syringe, evincing high internal capsule pressure, were processed for analysis.

2.3. Run products

All recovered capsules contained aqueous fluid and a single glass bead. Synthetic fluid inclusions were trapped as glass-hosted fluid inclusions, formed as the melt cooled through the glass transition temperature, Tg (cf. Romano et al., 1994; Simon et al., 2007a). The glass-hosted fluid inclusions were present as discrete phases at run conditions prior to quenching and do not represent fluids formed during quench (Simon et al., 2007a). Fluid inclusions were homogeneously distributed in the recovered glass (Fig. 1). Low-density vapor fluid inclusions contain a vapor bubble surrounded by liquid and in some inclusions contain a small opaque particle. These particles are inferred to be elemental silver owing to their bright white color when viewed under reflected light. The ratio of liquid to vapor in two-phase low-density vapor inclusions and the size of the vapor bubble are approximately constant in all runs. High-density brine fluid inclusions contain a vapor bubble, liquid, multiple salt crystals, typically one or more opaque particles, hypothesized to be silver based on their color when viewed under reflected light.

2.4. Run product analysis

2.4.1. Analyses of experimental glasses

Glass samples were analyzed by using wavelength dispersive spectrometry (WDS) electron probe microanalysis (EPMA). The EPMA operating conditions for major elements and Cl were: 15 kV accelerating potential, 5 nA beam current, and a 15-µm diameter beam with a minimum counting time of 20 s (sum of peak and background). Glass homogeneity was evaluated by performing multiple rim-torim line traverses on each glass. No Na diffusion was observed during the analyses (cf. Morgan et al., 1996; Acosta-Vigil et al., 2003). Yellowstone rhyolite (National Museum of Natural History, NMNH 72854 VG568) was used as the standard for Si, Al, Na and K. Kakanui hornblende and scapolite (Meionite, Brazil, USNM R6600-1) were used to standardize Fe and Cl, respectively. Detailed information for standards can be found in Jarosewich et al. (1980).

The concentrations of Pt in silicate glasses and glasshosted fluid inclusions were quantified by using LA-ICP-MS. We used the system at the IGMR, ETH Zurich, consisting of an energy-homogenized (Microlas), pulsed 193-nm ArF Excimer laser (Compex 110i, Lamda Physik) that enables controlled ablation (Günther et al., 1997, 1998; Heinrich et al., 2003) combined with an Elan6100DRC quadrupole ICPMS (Perkin Elmer). Laser ablation was performed in a 1-cm³ ablation chamber and monitored with a video camera that permitted constant observation of the sample surface during ablation. Instrument settings were similar to those reported in Pettke et al. (2004). In all runs, several large-beam (i.e., 90 µm spot size) analyses were performed on each glass with analyses spread across the glass bead from rim to rim; no compositional gradients for any elements were detected. In addition to these large-beam analyses, the Pt concentrations of glass volumes directly above and below analyzed fluid inclusions were quantified. Thus, the Pt solubility in glass data reported here reflect between 10 and 20 analyses per experimental glass. The silicate glass reference standard NIST SRM-610 was used as the standard to reduce all LA-ICP-MS data. The EPMA-determined Al2O3 concentration in glass was used as the internal standard. The transient signal for each analysis was integrated, and element ratios (e.g., Pt:Na) were quantified using the NIST-610 standard. The choice to use Al₂O₃ as the internal standard was based on its ability, at the 2σ level, to reproduce the EPMA-determined abundances of Na, K and Si in each glass.

2.4.2. Absence of silver-platinum alloy

Solubility experiments require that the activity of Pt in the charge remain at unity during the entire experiment. The use of Ag and AgCl to buffer the HCl concentration of the aqueous fluids introduces potential complications if



Fig. 1. (a) Photomicrographs of a recovered experimental glass bead with fluid inclusions; scale bar is 500 µm. (b) Photomicrograph of vapor inclusion hosted in glass; scale bar is 20 µm. (c) Photomicrograph of brine inclusion hosted in glass; scale bar is 30 µm.

Ag and Pt alloy during the runs. The phase diagram for the silver-platinum binary system indicates that Ag and Pt form a single alloy Ag₁₅Pt₁₇ at temperatures from 400 to 803 °C at atmospheric pressure (Okamoto, 1997). At temperatures ≥803 °C a broad solvus extends from 30 atomic% Ag and 93.9 atomic% Pt at 803 °C to 40.0 atomic% Ag and 87.0 atomic% Pt at 1188 °C indicating that Ag and Pt are immiscible over this temperature range. The hot spot of experimental capsules was 800 °C and the cold and hot ends were 798 °C and 803 °C, respectively. We analyzed the capsule material from several runs by using EPMA and observed a heterogeneous distribution of Ag along the interior walls of the Pt capsule with the majority of analyses indicating only the presence of Pt. This finding does not in itself rule out the presence of Ag-Pt alloy at run conditions which would reduce the activity of Pt resulting in an underestimation of the solubility of Pt in all system components. We interpret the heterogeneous distribution of Ag in the Pt capsule, coupled with data from the Ag-Pt binary join, indicating that the smallest concentration of Pt in Ag-Pt at run conditions is 94%, to suggest that any deviations in the activity of Pt are sufficiently small, certainly within the experimental uncertainties, so as to affect inconsequentially the results of the present study.

2.4.3. Fluid inclusion microthermometry

Following EPMA, the carbon coat was removed by diamond polishing and all probe mounts were cut into wafers on the order of 1 mm thick to expose glass on both sides. Individual fluid inclusions in glass range in size from ~ 10 to $\sim 100 \,\mu\text{m}$ with the majority of fluid inclusions in the 10 to 30 µm range. A USGS-type, gas-flow heating-freezing stage (Fluid, Inc.) was used to measure Tmice (final melting temperature of ice) and Td_{NaCl} (final dissolution temperature of NaCl; Bodnar and Vityk, 1994). The thermocouple was placed directly on top of the sample to prevent sample movement and to minimize the distance between the thermocouple and fluid inclusions; both serve to decrease uncertainties in temperature measurements. The heatingfreezing stage was calibrated at -56.6 °C (pure CO₂ melting temperature), 0 °C (pure H₂O melting temperature) and 374.1 °C (pure H₂O critical temperature). Uncertainties in Tm_{ice} and Td_{NaCl} were estimated to be ± 0.2 °C and ± 1.5 °C, respectively, based on replicate measurements of individual fluid inclusions.

2.4.4. LA-ICP-MS analyses of fluid inclusions

The concentrations of Na, K, Fe and Pt in individual fluid inclusions were quantified by using LA-ICP-MS and the standard SRM-610 from NIST as the external standard and microthermometrically determined Na as the internal standard. All analyzed fluid inclusions yielded microthermometrically determined bulk salinities which are consistent with expected salinities based on known phase relations in the NaCl-KCl-HCl-H2O system (Roedder, 1984; Sterner and Bodnar, 1984; Bodnar and Sterner, 1985; Bodnar et al., 1985; Bodnar and Sterner, 1987; Chou, 1987b; Sterner et al., 1988, 1992; Vanko et al., 1988; Chou et al., 1992; Anderko and Pitzer, 1993; Bodnar and Vityk, 1994). Glass-hosted fluid inclusions from multiple regions

of each glass were analyzed to evaluate chemical homogeneity. The diameter of the laser beam was set slightly greater than the maximum diameter of each fluid inclusion such that the entire fluid inclusion was ablated together with a minimal volume of surrounding matrix glass. The transient signal was deconvoluted and processed to remove the addition of elements present in the host from the fluid inclusion signal interval such that the reported composition of the fluid inclusion represents only those elements contained in the fluid inclusion with no contribution from the host (cf. Heinrich et al., 2003). A dwell time of 10 ms was used for Si. Al. Na. K and Fe. The dwell time for Pt was 20 ms. These short dwell times ensure representative sampling of the short, transient signals (Pettke et al., 2000) from glasshosted inclusions. The transient signal for each analysis was integrated, and element ratios (e.g., Pt:Na) were quantified using SRM-610. Element ratios determined by LA-ICP-MS were transformed into absolute element concentrations using Na as the internal standard. Absolute concentrations of Na in each fluid inclusion were determined by correcting the microthermometrically-determined wt.% NaCl eq. for the presence of KCl, AgCl and FeCl2 via the equation $NaCl_{true} = NaCl_{equiv} - 0.5 \times \Sigma X^{n+}Cl_n$ which assumes that all major cations in the fluid inclusion were present as chloride salts (Heinrich et al., 2003). The use of Na as an internal standard has been evaluated previously (Heinrich et al., 2003; Simon et al., 2007a). The absence of sulfur as a Pt-complexing ligand justifies this assumption. It is critical to note that element ratios, hence partition coefficients, are independent of this assumption and, therefore, the use of partition coefficients and exchange equilibria to evaluate Pt mobility is justified. Data reduction followed procedures outlined in Longerich et al. (1996) and Günther et al. (1998).

2.4.5. HCl concentration of volatile phases

The fugacity of HCl, f_{HCl} , was buffered in the runs at 140 MPa owing to saturation with elemental Ag and AgCl. The f_{HCl} can be described by the equilibrium

$$Ag^s + HCl^{mvp} = AgCl^{mvp} + 0.5H_2 \tag{1}$$

where mvp stands for magmatic volatile phase and s for solid The value for the equilibrium constant for Eq. (1) is 0.6. The activities of Ag^s and $AgCl^s$ are unity and the value for f_{H_2} is 6.2 bars at 140 MPa; f_{H_2} was calculated by using equations of Huebner and Sato (1970) and Belonoshko et al. (1992). These data yield a value for f_{HCl} equal to 4.1 bars. The fugacity of water, f_{H_2O} , at 140 MPa is 1147 bars and the molar ratio of HCl to H₂O, according to the Lewis and Randall rule, is 4×10^{-3} yielding a calculated log HCl concentration (wt.%) in the vapor at 140 MPa of 4. The lower pressure runs did not contain AgCl. To calculate the concentration of HCl in volatile phases at 100 MPa and brine at 140 MPa, we used the equation

$$\log \frac{NaCl^{mvp}}{HCl^{mvp}} = \log \frac{1}{K_{H/Na}^{mvp/m}} \times \frac{C_{Na}^{m}}{\sum Alkalies^{melt}(ASI-1)},$$
 (2)

from Williams et al. (1997) where ASI is the aluminum saturation index of the melt (i.e., the molar ratio $Al_2O_3/(Na_2O + K_2O))$ and $K_{H/Na}^{mvp/m}$ is defined as

$$K_{H/Na}^{mvp/m} = \frac{(C_H^{mvp} \times C_{Na}^{melt})}{(C_H^{melt} \times C_{Na}^{mvp})}$$
(3)

(Holland, 1972). Model values for $K_{H/Na}^{mvp/m}$ were taken from Williams et al. (1997). The calculated log HCl concentrations in vapor and brine are 3.7 wt.% and 4.8 wt.% at 140 MPa, respectively. At 100 MPa, the average HCl concentrations in vapor and brine are 0.8 wt.% and 1.6 wt.%, respectively.

3. RESULTS

3.1. Felsic melt

3.1.1. Major element and Cl concentrations of the melt

The elemental compositions of experimental glasses are provided in Table 1. The calculated aluminum saturation index (ASI = the molar ratio of $Al_2O_3/(Na_2O + K_2O))$ ranges from 1.19 to 1.31 indicating that all glasses are peraluminous. Most magmas associated with porphyry-ore deposits have ASI values that are below those of the melts in this study. Future experiments will be performed to evaluate the effect of melt composition (i.e., ASI) on Pt partitioning. The decrease in the Na₂O concentration of the quenched melt, relative to the starting melt, results from the exchange of Na in the melt for H in the volatile phases (vapor + brine). The concentration of K₂O does not change systematically which suggests that K₂O is not affected in a similar fashion to Na₂O. This effect has been documented in other studies of melt – volatile phase equilibria (Frank et al., 2002). EPMA glass totals on the order of 94-96 wt.% are consistent with the expected water solubility of 4-6 wt.% in rhyolite melt at 100-150 MPa (McMillan and Holloway, 1987).

3.1.2. Platinum solubility in felsic melt

The concentrations of Pt in silicate glasses (Table 1) exhibit more variability than major elements and Cl.

The low and high Pt concentrations ($\pm 2\sigma$ of the mean) at 140 MPa are $0.17 \pm 0.6 \,\mu\text{g/g}$ and $0.53 \pm 0.18 \,\mu\text{g/g}$ yielding an average of $0.28 \pm 0.26 \,\mu\text{g/g}$. The Pt concentrations ($\pm 2\sigma$) at 100 MPa are $0.33 \pm 0.05 \,\mu\text{g/g}$ and $0.42 \pm 0.13 \,\mu\text{g/g}$ yielding an average of $0.38 \pm 0.12 \,\mu\text{g/g}$. Several previous studies of metal solubility in silicate melts have pointed out that metal nuggets (at the sub-micron scale) may be present in quenched silicate melts and that incorporation of these nuggets into the LA-ICP-MSanalyzed volume of glass may artificially increase the measured solubility value (cf. Borisov and Palme, 1997; Ertel et al., 1999; Fortenfant et al., 2003; Cottrell and Walker, 2006; Simon et al., 2007b). We evaluated each LA-ICP-MS transient signal for the presence of Pt nuggets, typically indicated by a several-order of magnitude jump above glass background in the Pt transient signal, and noted their presence in approximately 5% of all analytical signals. Manually removing a nugget from a transient glass signal results in a decrease in the calculated Pt concentration of the melt of at most one order of magnitude. Retaining a Pt nugget during data reduction increases the calculated Pt concentration of the melt by no more than 20 percent. Inspection of all transient signals in this study indicates that there is no correlation between the number of Pt nuggets in silicate melt and the reported concentration of Pt in the melt. Thus, in the absence of definitive evidence that the entire mass of each Pt nugget was a stable phase at run conditions, we included Pt nuggets during signal processing. We note that if the Pt nuggets were present at run conditions (i.e., they were not produced on quench; Cottrell and Walker, 2006; Simon et al., 2007b), then our decision to retain nuggets during signal processing increases slightly (i.e., by no more than a few percent) the reported solubility of Pt in silicate melt and, thus, underestimates the vapor/melt and brine/melt partition coefficients. Hence, modeling results discussed below place a minimum on the Pt-scavenging ability of both vapor and brine.

Table 1

Concentrations of major elements (EPMA), Cl (EPMA) and Pt (LA-ICP-MS) in the run product glasses.

Concer		i major element	s (Li 1017), ci (l	in the second seco		le run product gia	3303.		
Run No.	Time (h)	SiO ₂ wt.% (±2σ)	$\begin{array}{c} K_2 O \ wt.\% \\ (\pm 2\sigma) \end{array}$	$Na_2O wt.\%$ (±2 σ)	FeO wt.% (±2σ)	$\begin{array}{c} Al_2O_3 \text{ wt.\%} \\ (\pm 2\sigma) \end{array}$	Cl wt.% (±2σ)	Pt $\mu g/g$ ($\pm 2\sigma$)	Total
140 MI	Pa runs								
4	206	76.10 (0.90)	3.93 (0.20)	2.80 (0.13)	0.05 (0.05)	11.57 (0.44)	0.16 (0.01)	0.27 (0.10)	94.57
5	110	76.45 (0.53)	3.77 (0.09)	2.73 (0.07)	0.03 (0.03)	11.14 (0.24)	0.14 (0.01)	0.53 (0.18)	94.23
6	377	75.87 (0.55)	3.88 (0.05)	3.05 (0.11)	0.04 (0.03)	11.90 (0.36)	0.11 (0.01)	0.17 (0.6)	94.82
7	205	76.35 (0.29)	4.98 (0.09)	2.24 (0.10)	0.05 (0.03)	11.43 (0.14)	0.14 (0.01)	0.30 (0.20)	95.17
8	111	75.72 (0.50)	4.28 (0.47)	2.45 (0.27)	0.05 (0.02)	11.42 (0.24)	0.14 (0.02)	0.20 (0.10)	94.86
14	160	75.69 (0.37)	4.85 (0.13)	2.39 (0.14)	0.04 (0.05)	11.23 (0.34)	0.16 (0.01)	0.20 (0.06)	94.33
Mean		76.09 (0.16)	4.28 (0.15)	2.64 (0.08)	0.04 (0.01)	11.45 (0.08)	0.14 (0.01)	0.28 (0.26)	94.92
100 MI	Pa runs								
15	159	76.32 (0.92)	4.08 (0.37)	3.00 (0.20)	0.03 (0.02)	12.01 (0.58)	0.15 (0.02)	0.42 (0.13)	95.59
16	564	76.41 (0.88)	4.39 (0.16)	3.05 (0.33)	0.03 (0.05)	11.73 (0.58)	0.14 (0.02)	0.33 (0.05)	95.75
Mean		76.37 (0.12)	4.24 (0.44)	3.03 (0.08)	0.03 (0.00)	11.87 (0.20)	0.15 (0.02)	0.38 (0.12)	

Uncertainties are presented as twice the standard deviation $(\pm 2\sigma)$ for the replicate measurements. Each reported oxide concentration represents the average of 10 to 30 spot analyses in different areas of each experimental glass. The Pt concentrations represent the average of large laser spot sizes (75 or 90 µm) which were used to ablate glass volumes which contained no fluid inclusions and also the glass volumes directly above and below ablated glass-hosted fluid inclusions.

3.2. Vapor and Brine

The concentrations of HCl, Na and K in aqueous vapor and brine fluid inclusions are presented in Table 2. Major element concentrations and bulk salinities are consistent with published phase relations in the NaCl-KCl-H2O system. The data indicate that the Na/K ratio of the aqueous fluids increased during the experiment owing to the exchange of H and K from the aqueous fluid for Na in the melt. This is also reflected in the decreased Na concentration of the melt. Fig. 2 shows the transient analytical signal for a representative glass hosted fluid inclusion. The signals for Na, K and Pt parallel one another in the glass and during the ablation of the fluid inclusion; this indicates that the Pt is contained within the fluid inclusion and not present as a particle at the glass-fluid inclusion interface. The concentration data for Pt in vapor and brine at 140 MPa and 100 MPa are presented in Tables 3 and 4, respectively. The Pt concentration of each ablated fluid inclusion is presented separately and an average Pt solubility in vapor and brine is calculated for each run. The average measured Pt solubilities $(\pm 1\sigma_{\bar{x}})$ in vapor at 140 (44 fluid inclusions) and 100 MPa (14 fluid inclusions) are $0.91 \pm 0.29 \,\mu g/g$ and $0.37 \pm 0.17 \,\mu\text{g/g}$, respectively. The average measured Pt solubilities $(\pm 1\sigma_{\bar{x}})$ in brine at 140 (33 fluid inclusions) and 100 MPa (13 fluid inclusions) are $16 \pm 10 \,\mu\text{g/g}$ and $3.3 \pm 1.0 \,\mu\text{g/g}$, respectively. Notwithstanding scatter in the data, discussed with respect to equilibrium in Section 3.3, the data indicate that Pt solubility in (S-free) aqueous vapor is lower than Pt solubility in (S-free) brine. This finding is consistent with the solubility behavior of other transition row metals (e.g., Au; Simon et al., 2005) wherein metal sol-

Table 2 LA-ICP-MS data for fluid inclusions from all experiments.

ubility is controlled by the concentration of HCl in the aqueous fluid (see Section 4.1; cf. Frank et al., 2002) which is higher in the brine relative to the vapor in the current set of experiments. Future experiments are planned to elucidate the effect of S on Pt partitioning.

3.3. Demonstration of equilibrium

The most important aspect of any experimental study is that equilibrium, or at least a trend toward steady-state conditions, can be demonstrated. Previous studies performed to quantify metal solubilities in immiscible aqueous fluids at magmatic conditions have trapped the aqueous fluids as fluid inclusions in pre-fractured quartz phenocrysts (e.g., Hanley et al., 2005; Simon et al., 2005, 2006; 2007a,b, 2008). Major effort in these studies was dedicated to demonstrate that the aqueous fluids had reached equilibrium with all system components prior to entrapment as fluid inclusions. In most studies, the major element solutes in the aqueous fluids appear to reach equilibrium rather quickly. This is based on microthermometrically determined bulk salinity data that are consistent with predictions based on known phase relations in the NaCl-KCl-H₂O system (Sterner and Bodnar, 1984; Bodnar and Sterner, 1985, 1987; Bodnar et al., 1985; Chou, 1987a; Sterner et al., 1988, 1992; Anderko and Pitzer, 1993; Bodnar and Vityk, 1994). The equilibrated nature of the major element load of trapped fluid inclusions has been taken as a priori evidence that the entire solute load of each fluid inclusion represents equilibrium. However, this may not be the case for transition row metals owing to the likely differences in

Run No.	Type of	^a N	^b Bulk wt.% NaCl	°Final wt.% NaCl	^d HCl wt.% (±	Na wt.%	K wt.% $(\pm 2\sigma)$
	inclusion		eq.	eq.	2σ)	$(\pm 2\sigma)$	
140 MPa r	uns						
4	Vapor	11	20	8.3-8.9	4.3 (0.8)	25 (0.2)	1.7 (0.2)
	Brine	6		41–44	7.4 (0.1)	79 (1.1)	66 (1.1)
5	Vapor	7	20	8.5-9.7	4.3 (0.4)	25 (0.2)	13 (0.2)
	Brine	4		42-46	6.9 (0.1)	77 (0.8)	55 (0.8)
6	Vapor	8	20	9.1–9.4	3.9 (0.4)	22 (0.4)	12 (0.3)
	Brine	7		42–44	4.8 (0.1)	84 (2.9)	47 (2.7)
7	Vapor	4	20	8.7–9.3	2.9 (1.0)	24 (0.1)	14 (0.4)
	Brine	3		42–44	4.3 (0.2)	90 (0.2)	11 (3.1)
8	Vapor	5	20	8.1–9.3	1.1 (0.2)	21 (0.3)	18 (0.2)
	Brine	5		41–45	2.5 (0.32)	86 (0.6)	82 (24)
14	Vapor	9	20	8.5-9.3	2.6 (0.9)	24 (1.6)	23 (0.2)
	Brine	8		41–43	3.6 (0.2)	87 (0.3	98 (0.9)
100 MPa r	uns						
15	Vapor	7	5.5	1.4-2.2	1.1 (0.2)	0.7 (0.03)	0.2 (0.02)
	Brine	4		64–67	2.0 (0.6)	80 (18)	46 (1.0)
16	Vapor	7	5.5	1.5-2.0	0.5 (0.15)	0.4 (0.09)	0.23 (0.03)
	Brine	9		61–65	1.1 (0.34)	80 (14)	63 (1.3)

^a Total number of inclusions analyzed by LA-ICP-MS.

^b Bulk salinity of the initial starting aqueous solution added to the charge.

^c Final measured range of salinities, expressed as wt.% NaCl eq., as determined by microthermometry following Bodnar and Vityk (1994).

^d HCl concentrations calculated following Williams et al. (1997).



Fig. 2. LA-ICP-MS transient signal of a glass-hosted fluid inclusion analysis. A laser spot size of $60 \,\mu\text{m}$ was used to ablate the 50 μm vapor inclusion and host glass. The intensities for Na, K and Pt parallel one another in the glass (i.e., quenched melt) and fluid inclusion suggesting that the Pt is contained within the fluid inclusion.

the diffusivities, which control fundamentally the rate of equilibrium, of transition row vs. alkali and alkaline earth metals in the melt and the fact that the aqueous fluid starts with a composition closer to its equilibrium state. In the current study, to avoid potential problems with the pre-fractured quartz technique, we equilibrated Pt metal (sourced from the Pt capsule), felsic silicate melt, aqueous vapor and aqueous brine and sampled the aqueous fluids at run conditions by trapping them as glass-hosted fluid inclusions in the melt as the melt passed through the glass transition temperature (Tg). Based on the quench rate for the cold-seal René vessel, the Tg for water-saturated rhyolite is on the order of 400 °C (Dingwell, 1998; Sowerby and Keppler, 1999) and the time to cool from run temperature through the Tg is on the order of 30 seconds. The salinity of the aqueous fluid(s) in the current sets of experiments is dominated by NaCl, KCl and HCl. The time required for the aqueous fluid(s) to reach equilibrium with respect to the major element solutes is controlled the exchange of these elements between the fluid and silicate melt which is controlled by diffusion in the melt. Published experimental studies suggest that this occurs in a matter of three to four days, possibly in only a few hours based on the small diffusion lengthscale required in the 2 mm diameter melt (Carmichael and Mackenzie, 1963; Thompson and Mackenzie, 1967; Bailey et al., 1974, Bailey and Cooper, 1978; Scaillet and MacDonald, 2001). The run times in the current study ranged at 140 MPa from 4.25 to 16 days and at 100 MPa from 7 to 24 days. We suggest, based on our own experience and published data, that these times are sufficient for the system to reach equilibrium and this is borne out by the small uncertainties in measured concentrations of all elements in the melt and major elements in the aqueous fluids. The equilibrated

nature of Pt in the melt, ranging from 170 to 530 ng/g at 140 MPa and 330 to 420 ng/g at 100 MPa, suggests that the aqueous fluids should have reached equilibrium as diffusion in the very low viscosity aqueous fluids is assumed to be significantly faster than the more viscous H_2O -saturated rhyolite melt.

The entrapment of fluid inclusions in silicate melt as the melt passes through the Tg indicates that the fluids were in equilibrium with the system until the run was terminated. In turn, this should lead to a small range in LA-ICP-MS-measured Pt solubilities in the aqueous fluids and the invariance of calculated Nernst-type partition coefficients as a function of run time could be used as the criteria to evaluate equilibrium as has been done in numerous previous studies (e.g., Candela and Holland, 1984; Webster, 1992; Gammons et al., 1992; Gammons and Bloom, 1993; Gammons et al., 1993; Gammons, 1995, 1996; Gammons and Williams-Jones, 1997; Jugo et al., 1999; Archibald et al., 2001, 2002; Frank et al., 2002; Simon et al., 2004, 2005, 2006, 2007a,b; Rempel et al., 2006; Zezin et al., 2007). However, in the current study the measured Pt solubility values for a small number of fluid inclusions at each pressure deviate by up to two orders of magnitude from the calculated mean solubility value for a given run, calculated including all solubility measurements. Inclusion of these seemingly outlier data and propagation of the resultant uncertainties for Pt solubility in vapor and brine through Nernst-type partition coefficient (i.e., $D_{Pt}^{i/j}$) calculations results in uncertainties in $D_{\rm Pt}^{i/j}$ that approach, in some cases, the mean partition coefficient for the run, as presented and discussed in Section 3.4. For example, the lowest and highest measured Pt concentrations in aqueous vapor from run 4 at 140 MPa are $0.07 \,\mu g/g$ and $2.17 \,\mu g/g$, respectively. The mean Pt concentration $(\pm 1\sigma_{\bar{x}})$ in aqueous vapor from run 4 is $0.88 \pm 0.40 \,\mu\text{g/g}$. There were no anomalous Pt spikes in the transient signal that yielded the higher calculated Pt concentration. Applying a 3σ criterion, both the low and high measured concentrations from this run could be disregarded, but we choose to include them as we have no quantitative constraint on why they are outliers. Inspection of the measured Pt concentrations from other runs indicates that similar "outliers" are present in a total of 3 runs; all other runs yield Pt solubility data that are internally consistent to within approximately one order of magnitude. One hypothesis for the apparently low and high measured concentrations in the 3 runs involves diffusive loss or gain of Pt by the fluid inclusion during quench. The high concentration may represent accidental entrapment of a Pt nano-nugget. The latter is not observed in the transient signal although we recognize that the mass of Pt required increasing the measured Pt concentration from the mean of 0.88 μ g/g to 2.17 μ g/g is sufficiently small and may simply be undetectable in the transient signal.

During quench, the solubility of Pt in the melt is expected to decrease with decreasing temperature. This may cause down-temperature exsolution of Pt from the melt may lead to the formation of Pt nano-nuggets in the melt as discussed above (Section 3.1.2). There are no

Table 3 Measured concentrations $(\pm 1\sigma_{\bar{x}})$ of Pt in individual vapor and brine fluid inclusions at 140 MPa.

	$C_{ m Pt}^v$	C_{Pt}^b
Run 4		
	0.17	5.18
	0.43	3.50
	1.31	1.85
	2.17	3.43
	0.07	5.18
	1.29	5.10
	0.40	
	1.80	
Mean	0.88	3.35
1 sigma	0.20	0.70
Run 5		
	0.66	1.61
	0.16	1.65
	0.15	0.83
	1.31	9.74
	0.06	4.00
	3.88	
	0.15	
Mean	0.91	3.57
l sigma	0.52	1.63
Run 6		
	0.15	8.83
	0.06	9.12
	0.30	3.81
	0.15	9.3/
	0.07	4.//
	0.07	5.90
	0.27	25
Mean	0.15	9.6
1 sigma	0.03	2.8
n 7	0100	2.0
Run /	0.78	54.02
	0.78	54.02 76.06
	0.21	70.90
	1.5	5.25
Mean	1.67	45
1 sigma	0.93	22
D 9		
Kun o	0.52	38 49
	0.46	19.69
	0.48	10.43
	1.58	59.26
	0.58	15.99
Mean	0.72	29
1 sigma	0.21	9
Run 14		
	0.67	5.89
	0.43	2.84
	0.91	22.81
	0.08	3.88
	1.88	0.39
	2.22	4.43
	2.15	1.87
	0.93	7.89
Mean	1.1	6.3
1 adama a	0.6	2.5

Tal	ole	4
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Measured concentrations $(\pm 1\sigma_{\bar{x}})$ of Pt in individual vapor and brine fluid inclusions at 100 MPa.

	$C_{ m Pt}^v$	$C_{ m Pt}^b$
Run 15		
	0.03	0.73
	0.03	4.79
	0.27	3.15
	0.08	0.65
	0.18	
	0.21	
	0.59	
Mean	0.20	2.33
1 sigma	0.07	1.01
Run 16		
	0.06	2.75
	0.44	0.81
	0.99	1.42
	0.19	0.76
	0.13	5.25
	1.42	2.24
	0.54	1.0
		7.7
		2.2
Mean	0.54	2.7
1 sigma	0.19	1.72

available data that constrain the relationship between decreasing temperature and Pt solubility in aqueous fluids at magmatic-hydrothermal conditions, but it is likely that Pt solubility in the aqueous fluid decreases with decreasing temperature. If Pt exhibits retrograde solubility in the aqueous fluids, then a chemical potential gradient should cause Pt to diffuse from the melt into the fluid inclusions which would cause an increase in the measured solubility values. This may explain the measured "high" concentrations measured in some fluid inclusions; however, this does not explain the seemingly anomalous "low" solubility values measured for some fluid inclusions in 3 run product glasses. Testing this hypothesis requires the ability to sample glass surrounding the fluid inclusion at sufficient high spatial resolution to extract diffusion profiles, if in fact diffusion from the melt (or vice versa) is responsible for the measured low and high solubility values. This may be possible with nano-SIMS, but is outside the scope of the present study. We suggest that the present data set has sampled a sufficient number of glass-hosted fluid inclusions to warrant confidence that the reported mean solubility values accurately constrain the solubility of Pt in both aqueous vapor and aqueous brine at run conditions and that equilibrium was attained and preserved in all phases in quenched run products in all experiments. For example, removing those data that fall outside of 3σ of the average Pt concentration measured for vapor fluid inclusions in run 4 results in an average Pt solubility of $0.81 \pm 0.24 \,\mu\text{g/g}$. This mean value is not statistically different than the mean calculated with all data; i.e., $0.88 \pm 0.40 \,\mu\text{g/g}$. We plan to incorporate nano-analysis of the glass surrounding fluid inclusions in future studies

Table 5 Calculated Nernst-type partition coefficients $(\pm 1\sigma_x)$ for Pt between coexisting vapor, brine and melt.

Run #	$D_{ m Pt}^{v/m}$	$D_{ m Pt}^{v/m}$	$D_{ m Pt}^{v/b}$
140 MPa			
34	3.2 (1.5)	12 (4)	0.27 (0.13)
5	1.7 (1.3)	6.7 (3.4)	0.25 (0.23)
6	0.88 (0.33)	57 (23)	0.02 (0.01)
7	6 (3)	149 (67)	0.04 (0.02)
8	3.7 (1.3)	145 (53)	0.03 (0.01)
14	5.5 (2.0)	31 (18)	0.18 (0.12)
Mean	2.9 (1.0)	67 (27)	0.13 (0.05)
100 MPa			
15	0.47 (0.23)	5.6 (2.4)	0.1 (0.05)
16	1.6 (0.75)	8.1 (7.1)	0.2 (0.13)
Mean	1.0 (0.2)	9.2 (0.4)	0.15 (0.05)

to constrain the local environment of the melt during quench.

3.4. Calculated Nernst-type partition coefficients

The Pt solubility data (Section 3.2) were used to calculated Nernst-type partition coefficients for Pt between vapor and melt $(D_{Pt}^{v/m})$, brine and melt $(D_{Pt}^{b/m})$ and vapor and brine $(D_{Pt}^{v/b})$. These data are presented in Table 5. The mean values for $D_{Pt}^{v/m}$ ($\pm 1\sigma_{\bar{x}}$) at 140 and 100 MPa are 2.9 \pm 1.0 and 1.0 \pm 0.2, respectively. The values for $D_{Pt}^{b/m}$ ($\pm 1\sigma_{\bar{x}}$) at 140 and 100 MPa are 6.1 \pm 2.4, respectively. The values for $D_{Pt}^{v/b}$ ($\pm 1\sigma_{\bar{x}}$) at 140 and 100 MPa are 0.13 \pm 0.05 and 0.15 \pm 0.05, respectively. Changes in e.g., pressure, temperature, gas fugacities, bulk composition will cause the partition coefficients to change; thus, caution should be exercised when extrapolating these values to sets of conditions different from those employed in our experiments.

4. DISCUSSION

4.1. Comparison to extant data

Hanley and Heinrich (2007) report solubility data for Pt in hydrous salt melt (75 wt.% $CaCl_2 + MgCl_2$, 25 wt.% H₂O) equilibrated experimentally with either Pt metal or sperrylite (PtAs₂). The a_{HCl}^{brine} was buffered by using tremolite-diopside-enstatite-quartz. The solubility of Pt in the salt melt, equilibrated with Pt metal, is $14.4 \pm 6.7 \,\mu\text{g/g}$. The solubility of Pt in the salt melt, equilibrated with sperrylite, is $4.6 \pm 1.9 \,\mu\text{g/g}$. Hanley et al. (2005) report Pt solubility values for 20 and 70 wt.% NaCl eq. brine, trapped at 800 °C and 150 MPa, that range from 330 to $4556 \,\mu\text{g/g}$ at 70 wt.% NaCl eq. and from 4 to 469 µg/g at 50 wt.% NaCl eq. The measured Pt solubilites reported in Hanley et al. (2005) yield Nernst-type partition coefficient values for Pt between brine and silicate melt, $D_{Pt}^{brine/melt}$, that range from 6.6×10^3 to 5.2×10^4 at 20 wt.% NaCl eq. and 1.0×10^2 to 2.6×10^4 at 70 wt.% NaCl eq. Their solubility values for Pt in brine decrease by nearly 2 orders of

magnitude as the salinity of the brine salinity increases from 20 to 70 wt.% NaCl eq. The solubility data for brine in the current study are consistent, within one order of magnitude, with the results published by Hanley and Heinrich (2007) and suggest that the data in Hanley et al. (2005) likely overestimate by up to two orders of magnitude the solubility of Pt in magmatic brine.

Ballhaus et al. (1994) experimentally studied the partitioning of Pt between sulfide phases, metal alloys and supercritical SiO₂-NaCl-saturated $H_2O \pm CH_4$ -CO₂-H₂S fluids at 900 °C and 1 GPa. They sampled the supercritical aqueous fluid at run conditions by trapping the fluid as quartz-hosted fluid inclusions. They used proton induced X-ray emission (PIXE) to measure metal concentrations in individual fluid inclusions and report Pt concentrations that range from below detection to several weight percent. The several order of magnitude variability in their measured Pt concentrations indicate that the trapped fluid inclusions sampled the supercritical fluid over a range of time at run conditions and, thus, interpreting the range of data is difficult. To our knowledge there are no other extant experimental data on Pt solubility in magmatic volatile phases; however, data from natural volcanic gases suggest that Pt mobility in magmatic aqueous fluids may be quite high.

4.2. Mass transfer of Pt between melt, vapor and brine

The measured Pt solubilities in silicate glasses at 140 and 100 MPa (i.e., from 6 to 4 km at lithostatic pressures), pressures over which magmatic volatile phases evolve from causative magmas in some porphyry environments (e.g., Butte; Rusk et al., 2008), suggest that decompression of a silicate melt does not affect the solubility of Pt in the melt. This behavior is opposite that reported for lanthanides (Urabe, 1985; Webster et al., 1989), Cu (Williams et al., 1995; Simon et al., 2006), Fe (Simon et al., 2004) and Ag (Simon et al., 2008) and suggests that increasing melt polymerization during decompression, owing to a decrease in the NBO/T of the melt during (Mysen, 1991), does not affect Pt solubility in the melt. The 3-fold increase in the vapor/melt partition coefficient as pressure increases from 100 to 140 MPa reflects the increased salinity, hence Cl concentration, of the vapor phase along the solvus as the total pressure increases toward the critical pressure, approximately 160 MPa at 800 °C. The same behavior is observed for Pt solubility in the brine. As pressure increases from 100 to 140 MPa, the salinity of the brine decreases from \sim 65 to ~42 wt.% NaCl eq., but the concentration of HCl increases several fold. These findings are consistent with transport of Pt as a Pt-Cl species in both vapor and brine. We suggest that Pt may be transported as PtCl₂ in both the brine and vapor based on solubility studies of other metals such as Cu (Candela and Holland, 1984; Williams et al., 1995; Simon et al., 2006), Fe (Chou and Eugster, 1977; Simon et al., 2005) and Au (Frank et al., 2002). The mass transfer of Pt from silicate melt to the volatile phase can be expressed by two possible equilibria which are variations of equilibria proposed by Hanley et al. (2005) based on the work of Frank et al. (2002):

$$PtO^{melt} + 3HCl^{mvp} = PtCl_3H_2^{mvp} + H_2O \tag{4}$$

$$PtO^{melt} + 2HCl^{mvp} = PtCl_2^{mvp} + H_2O$$
⁽⁵⁾

where mvp is magmatic volatile phase (i.e., vapor or brine). These equilibria assume that Pt is present as Pt^{2+} (i.e., PtO) in the melt. To our knowledge there are no data that constrain the speciation of Pt in silicate melt. Recent experimental work by Keller (2008) on the solubility of Pd in silicate melt indicates that Pd is present as both PdO_{0.5} and PdO, based on experiments in which Pd solubility was determined as a function of f_{O_2} , from $f_{O_2} = 1$ bar to 10^{-11} bars. The Pd solubility data, when plotted as the log of Pd concentration, in $\mu g/g$, vs. log f_{O_2} yield a slope of 0.36, which suggests both Pd¹⁺ and Pd²⁺ in the melt; a slope of 0.25 indicates Pd¹⁺ and a slope of 0.5 indicates Pd²⁺. If Pt is also present as Pt¹⁺ in the current experimental glasses, then the mass transfer of Pt from the silicate melt to the magmatic volatile phases could be written as the equilibria

$$PtO_{0.5}^{melt} + 0.25O_2 + 3HCl^v = PtCl^{mvp} + 0.5H_2O$$
(6)

$$PtO_{0.5}^{melt} + 0.25O_2 + 2HCl^{mvp} = PtCl_2H^{mvp} + 0.5H_2O.$$
 (7)

The speciation of Pt in the melt and volatile phase is not the focus of this study and Eqs. (4)–(7) simply illustrate likely Pt species based on extant experimental data for other metals. Eqs. (4)–(7) illustrate that changes in the a_{HCI} of the brine and vapor should affect the solubility of Pt in the volatile phase. The data reported here suggest that the increase in Pt solubility in the vapor phase as pressure increases from 100 to 140 MPa is a function of increasing a_{HCl}^{vapor} , consistent with data for other metals. The concentration of HCl in the vapor increases from 0.8 wt.% at 100 MPa to 3.7 wt.% at 140 MPa. The vapor/melt partition coefficients $(\pm 1\sigma)$ for Fe (Simon et al., 2004), Au (Simon et al., 2005) and Ag (Simon et al., 2008) increase from 0.3 (0.5) to 1.9 (0.25), from 10 (2) to 56 (16), and from 23 (5) to 32 (15), respectively, as pressure increases from 100 to 140 MPa. All these data are consistent with the positive relationship between a_{HCl} and Pt solubility.

The increase in the measured Pt solubility in the brine as pressure increases from 100 to 140 MPa is consistent with the increase in the a_{HCl}^{brine} . The concentrations of HCl in the brine at 100 and 140 MPa are 1.6 wt.% and 4.8 wt.%, respectively. Hanley et al. (2005) postulate that Pt-Cl species may be salted out of the brine during decompression owing to the increasing concentration of NaCl and concomitant drop in the a_{HCl}^{brine} . Their hypothesis is consistent with the Pt solubility data reported here. The new data indicate that the increased total salinity of the brine, as pressure decreases along the brine solvus, causes a decrease in the concentration of HCl in the brine. Examination of Eqs. (4)–(7) indicates that the drop in a_{HCl}^{brine} shifts these equilibria to the left resulting in the observed lower Pt solubility in brine. These data suggest that neutralization of brine during water rock reaction may be an important cause of Pt precipitation during decompression.

The experimentally determined vapor/brine partition coefficient value for Pt remains statistically unchanged as pressure drops from 140 to 100 MPa. On first inspection, this finding appears to be inconsistent with the thermodynamic requirement that the vapor/brine partition coefficient should decrease as the ratio of the critical pressure to the run pressure decreases. However, in the current set of experiments, the ratio of HCl in the vapor to that in the brine remains relatively constant as pressure is varied from 100 to 140 MPa. If the solubility of Pt is controlled strictly by the C_{HCl}^{fluid} , and not total salinity, then the results obtained here do not violate thermodynamic prediction.

4.3. The Pt-transporting capacity of vapor and brine

In order to translate the experimental Pt solubility and partitioning data to natural systems, we used the solubility data and partition coefficients to calculate the quantity of Pt that vapor and brine may scavenge from silicate melt and transport into the overlying porphyry environment. The calculations are based on work described in detail in Candela (1986) and also discussed in Cline and Bodnar (1991). The quantity of Pt which may be scavenged by a volatile phase and transported from the magma to the porphyry regime can be calculated by using the equation

$$E(\mathbf{Pt}) = \left[\frac{\mathbf{C}_{\mathrm{H_2O}}^{fluid,t=0}}{\mathbf{C}_{\mathrm{H_2O}}^{fluid,t=s}}\right]^{\overline{D}_{\mathrm{Pt}}} \times \left[1 + \frac{\overline{D}_{\mathrm{Pt}}}{\mathbf{C}_{\mathrm{H_2O}}^{fluid,t=s} \times D_{\mathrm{Pt}}^{v/m}}\right]^{-1}$$
(8)

if Pt solubility values for vapor, brine, melt and crystals are known. The variable E is the efficiency of Pt removal by either the vapor brine; i.e., the percentage of Pt that can be scavenged by the volatile phase from the melt. The equation allows one to model the effect of varying the initial water concentration of the melt $(C_{H_2}O^{fluid,0})$ to the concentration of water at water saturation (C_{H} , $O^{fluid,t=s}$); i.e., the water content required to drive the exsolution of a volatile phase from the silicate melt. The crystallization of sulfide or exsolution of a sulfide melt from the silicate melt is expected to have a significant effect on the Pt budget of the melt phase. To our knowledge there are no published data that constrain the partitioning of Pt between rhyolite melt and sulfide phases. Data from natural systems (cf. Peach et al., 1994) and experiments (cf. Fleet et al., 1991; Fleet and Stone, 1991) on more mafic assemblages (e.g., basalt melt and sulfides) at higher temperatures suggest that a reasonable partition coefficient for Pt between sulfide and rhyolite melt is on the order of 10^3 . Brenan et al. (2003) report an experimentally determined partition coefficient value of <0.009 for Pt between silicate melt and olivine suggesting that the effect of silicate phases on the Pt budget in rhyolite can be neglected in the model calculations performed here. Therefore, the model calculations used a $D_{pl}^{sulfide/sil.melt}$ value of 10^3 and the \overline{D}_{Pt} value was calculated by varying the modal abundance of sulfide from 0.1 to 1%. Eq. (8) assumes a constant $D_{Pt}^{i/j}$, a condition not necessarily valid for natural systems where $D_{Pt}^{i/j}$ will vary as a function of the concentrations of e.g., Cl, HCl, and H₂S. However, the calculations are meant simply to illustrate the Pt-scavenging capacity of vapor and brine which are evolved during progressive solidification of a silicate melt.

The values for E(Pt) were calculated by varying both the ratio of $C_{H_2O}^{fluid,t=0}$ to $C_{H_2O}^{fluid,t=s}$ (i.e., the initial water concentration and the water concentration at saturation) and the

modal proportion of sulfide. The data are presented in Table 6. The calculated efficiencies of Pt removal by a fluid, E(Pt), suggest that the initial water content of the melt and the modal abundance of sulfur in the solidification front both affect critically the ability of vapor and brine to scavenge Pt from the silicate melt. For example, for the vapor phase at 100 MPa, the E(Pt) increases from 0.005 to 0.18 as the ratio of $C_{H_2O}^{l,0}$ to $C_{H_2O}^{l,s}$ increases from 0.1 to 0.5 at a constant mass fraction of sulfide of 0.1%. If the initial ratio of $C_{H_2O}^{l,0}$ to $C_{H_2O}^{l,s}$ is held constant at 0.5, the E(Pt) for the vapor at 100 MPa decreases from 0.18 to 5.1×10^{-5} as the modal abundance of sulfide increases from 0.1 to 1%. Similar results were obtained for the brine. These model results indicate that higher initial water concentrations of the melt increase the Pt-scavenging ability of the vapor and brine unless the Pt budget is dominated by sulfide phases.

The E(Pt) data were used to calculate the total quantity of Pt that may be scavenged by vapor and brine from a crystallizing silicate melt. An initial Pt concentration of 1 ng/g in the silicate melt was used in all calculations. Increasing the initial Pt concentration of the melt in the model calculations would result in higher total quantities of Pt being scavenged by vapor and brine. However, the percentage of Pt removed, i.e., the variable E(Pt), is unchanged. The calculations were performed for melts equivalent to 10 km and 100 km equidimensional plutons These sizes are not meant to imply the intrusion of a single magma at one point in time and space, but rather the total, timeintegrated flux of melt in porphyry environments as documented in field studies (Arribas et al., 1995; Richards, 2005; Simmons and Brown, 2006). The quantity of Pt transported by vapor and brine remains relatively constant as pressure changes from 100 to 140 MPa. The data are presented in Table 6. For example, vapor evolved from a water-rich, sulfide-poor magma may transport a maximum of 4.8×10^{11} and 9×10^{11} grams (1.5×10^4 and 2.8×10^4 million Troy ounces) of Pt at 100 and 140 MPa, respectively. A brine evolving under the same conditions may transport a maximum of 9×10^{11} and 1.3×10^{12} g $(3.4 \times 10^4 \text{ and } 4.1 \times 10^4 \text{ million Troy ounces})$ of Pt at 100 and 140 MPa, respectively As mentioned above, increasing the modal abundance of sulfide and reducing the initial water content of the melt, thus allowing significantly more crystallization to occur to prior to degassing, results in small integrated quantities of Pt being removed from the melt by a volatile phase. Importantly, the model data indicate that the Pt-scavenging potential of vapor is similar to that of brine, consistent with the results of other recent studies of ore metal transport (cf. Williams-Jones and Heinrich, 2005).

4.4. Application to natural systems

The model results presented above are consistent with the reported Pt abundances of several "Pt-rich" porphyry deposits. Economou-Eliopoulos (2005) reports Pt concentrations of 3.4×10^6 , 3.7×10^6 and 1.5×10^6 grams (0.11, 0.12 and 0.05 million Troy ounces, respectively) for the Skouries (Greece), Elatsite (Bulgaria) and Santo Tommas (Philippines) porphyry deposits, respectively. The model data presented above suggest that the formation of Pt-rich porphyries are favored if the source magma is water and poor in sulfur, allowing for fluid saturation early in its differentiation history and prior to sulfide saturation. The data are consistent with the hypothesis that highly oxidized systems, where sulfide stability is minimized, could be targeted for elevated Pt concentrations in a porphyry environment. Platinum enrichment may also be favored in systems where sulfur is lost to the gas phase during early degassing of a CO_2 -rich fluid phase. In both of these scenarios, Pt concentrations of the silicate melt would remain high.

Caution should be always be exercised when applying experimental data to natural systems where the PTX conditions may be not be constrained to the degree as they are in the laboratory. The current study used a peraluminous melt. Many PGE-enriched porphyry deposits are associated with magmas of more alkalic character than the melt used in the current set of experiments (e.g., Werle et al., 1984; Mutschler et al., 1985; Hulbert et al., 1988; Mulja and Mitchell, 1991; Loney and Himmelberg, 1992; Cassidy et al., 1996; Ohnenstetter and Watkinson, 1998). This study was not designed to explore the effect of melt chemistry on Pt solubility and partitioning among silicate melt, vapor and brine. Increasing aluminosity of a silicate melt favors the exsolution of a more HCl-rich volatile phase(s); i.e., the HCl concentration of a magmatic volatile phase will be higher when the volatile phase is in equilibrium with a peraluminous melt and lower when the volatile phase is in equilibrium with a peralkaline melt. Accordingly, as seen in Eqs. (4)-(8), lower HCl concentration in the volatile phase will result in a decrease in the mass transfer of Pt from the silicate melt to the volatile phase. Thus, the partition coefficients calculated from the present data set may be expected to decrease. Future experiments are planned to test this hypothesis.

5. CONCLUSIONS

The solubility of Pt in rhyolite melt at 800 °C and $f_{O_2} \approx$ NNO is insensitive to pressure over the range of 100 to 140 MPa. Measured Pt solubilities in aqueous vapor and brine increase with increasing pressure along the limbs of the vapor-brine solvus from 100 to 140 MPa. This relationship is consistent with Pt solubility in magmatic aqueous fluids being controlled by the activity of HCl in the fluid, calculated to increase with increasing pressure, and indicates that the activity of HCl is a more important variable than total salinity. The Pt solubility data are used to estimate the total quantity of Pt that may be scavenged from the silicate melt by vapor and brine over the integrated lifetime of a silicic magmatic system as a function of both the initial water content of the melt and the modal abundance of sulfide that crystallizes during cooling (i.e., solidification). Model results suggest that timing of crystallizationdriven aqueous fluid saturation, controlled by the ratio of initial water content of the melt to the water content at saturation, and the modal abundance of sulfides in the crystal mush affect significantly the ability of vapor and brine to scavenge and transport Pt from the silicate melt. Conditions

Efficien	cles of removal (of Pt from the melt by	Aupor and onno and an damine				
$\frac{C_{H_2}^{1,0}}{C_{H_2}^{1,3}}$	Sulfide mass fraction %	$^{a}E(Pt)$ vapor	Grams of Pt scavenged by vapor from a 10 ³ km ³ pluton	Grams of Pt scavenged by vapor from a 10 ⁶ km ³ pluton	$^{a}E(Pt)$ brine	Grams of Pt scavenged by brine from a 10 ³ km ³ pluton	Grams of Pt scavenged by brine from a 10 ⁶ km ³ pluton
100 MF	a						
0.1	0.1	0.5	$1.4 imes 10^7$	$1.4 imes 10^{10}$	31	$8.5 imes 10^7$	$8.5 imes10^{10}$
0.5	0.1	18	$4.8 imes 10^8$	$4.8 imes 10^{11}$	41	$1.1 imes 10^9$	$1.1 imes 10^{12}$
0.1	1	$5.5 imes10^{-11}$	$1.5 imes 10^{-3}$	1.5	$4.4 imes 10^{-10}$	$1.2 imes 10^{-2}$	$1.2 imes 10^1$
0.5	1	$5.1 imes10^{-3}$	$1.4 imes 10^5$	$1.4 imes 10^8$	$3.1 imes 10^{-2}$	$8.3 imes 10^5$	$8.3 imes 10^8$
140 MF	a						
0.1	0.1	1.7	$4.5 imes 10^7$	$4.5 imes 10^{10}$	7.7	$2.1 imes 10^8$	$2.1 imes 10^{11}$
0.5	0.1	33	$9 imes 10^8$	$9 imes 10^{11}$	49	$1.3 imes 10^9$	$1.3 imes 10^{12}$
0.1	1	$2 imes 10^{-10}$	$5.3 imes10^{-3}$	5.3	$2.51 imes 10^{-9}$	$6.8 imes10^{-2}$	$6.8 imes10^1$
0.5	1	$1.6 imes10^{-2}$	$4.4 imes10^5$	$4.4 imes10^8$	$7.5 imes 10^{-2}$	$2.0 imes10^6$	$2.0 imes 10^9$

provoking early aqueous fluid saturation combined with low sulfide abundance favor greater efficiency of Pt transport. Silicate melts with average Pt concentrations are capable of supplying significant quantities of Pt to magmatichydrothermal fluids in Earth's upper crust.

ACKNOWLEDGMENTS

This work was partially supported by NSF EAR 0609550. ACS thanks Tim Grove for advice on experimental techniques related to PGE research and NSF for their encouragement of a new career PI. We thank Chris Heinrich for allowing us to use his LA-ICP-MS facility at the ETH, Zurich. Thomas Pettke gratefully acknowledges funding from the Swiss National Science Foundation.

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Associate editor: Edward M. Ripley