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## Platinum Solubility in High Temperature, Hypersaline Fluids: Preliminary Experimental Results and Application to Layered Intrusions

J.J. Hanley and J.E. Mungall

Department of Geology, University of Toronto, 22 Russell Street, Toronto, Ontario, M5S 3B1  
e-mail: hanley@geology.utoronto.ca

The solubility of Pt in high temperature (greater than 500°C), chloride-rich brines has not previously been evaluated experimentally. Petrographic and microthermometric studies undertaken in fluid-modified PGE (platinum group element) deposits have demonstrated evidence for the presence of early, hypersaline brines during Pt deposition or prior to this. Furthermore, salinities have been observed to peak in the ore-bearing horizons. In the Picket Pin deposit, Stillwater Complex (Hanley and Mungall, in prep.) and Merensky Reef, Bushveld Complex (Balhaus and Stumpfl, 1986; Johan and Watkinson, 1986) early stage CO<sub>2</sub>-rich and halite-rich inclusions have been identified within intercumulus quartz and feldspar which contain 60 wt% to greater than 90 wt% eq. NaCl. In both deposits, these hypersaline inclusions are absent from barren stratigraphy. In other deposits such as at Sudbury (North Range footwall deposits), early-stage, CaCl<sub>2</sub>-NaCl-(KCl)-(BaCl<sub>2</sub>)-(FeCl<sub>2</sub>)-(MnCl<sub>2</sub>)-rich inclusions trapped in granophyric veins and PGE-bearing quartz-chalcopryrite veins demonstrate salinities between 40 and 60 wt% eq. NaCl, approximately 4 to 6 times more saline than the ancient groundwaters circulating at depth in both deposits (Farrow, 1994; Molnar et al., 2002; Hanley and Mungall, in prep.). At the pressures and temperatures of entrapment in all of these examples, fluids were probably liquids (brines) rather than supercritical fluids, due to the effects of high salinity on the position of the critical point and size of the two-phase field in the H<sub>2</sub>O-NaCl and H<sub>2</sub>O-CaCl<sub>2</sub> systems.

The genetic origin of these deposits have been demonstrated by many researchers (Boudreau et al., 1986a,b; Balhaus and Stumpfl, 1986; Johan and Watkinson, 1986; Li, 1992; Farrow, 1994 and others) to be the result of hydrothermal or evolved fluid modification of primary magmatic PGE concentrations, but the relative importance of the magmatic vs. hydrothermal/evolved fluid processes have not been fully determined for the deposits in question. PGE solubility under the thermochemical conditions in fluids associated with the deposits has not been investigated experimentally, and therefore, the exact nature of the transportation and deposition fluid-modified portions of the ores is not known.

Furthermore, the behavior of the PGE in early-stage hypersaline fluids (or hydrated halide melts) is not known. These fluids were clearly present during magmatic differentiation and crystallization.

Indisputable experimental constraints on PGE solubility in moderately to slightly acidic (pH 4.6 ~ 5.5), moderately to very oxidizing (Ni-NiO to MnO<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub> buffer) supercritical fluid have been collected at lower salinity (less than 10 wt% KCl), lower temperature (400-500°C) conditions (Xiong and Wood, 2000). In these experiments, solubilities of Os and Pd were determined to range from approximately 10 to 10<sup>3</sup> ppb. For Os, order-of-magnitude changes in solubility were most sensitive to large changes in *f*O<sub>2</sub> and salinity. For Pd, the effects of decreasing *f*O<sub>2</sub> and pH on solubility were strongly counteracted by increasing temperature, confirming theoretical predictions that Pd solubility probably increases exponentially with increasing temperature.

In general, these are significant results because they demonstrate that theoretical predictions of PGE solubility at high T (Sassani and Shock, 1998) have underestimated actual values by several orders of magnitude. However, it has been suggested that these solubilities do not apply to the PGE-bearing layered intrusions described because the alteration assemblages within the PGE-bearing horizons are not consistent with the action of acidic and oxidizing fluids. Evidence of multiple fluid generations passing through the igneous stratigraphy (Balhaus and Stumpfl, 1986; Hanley and Mungall, in prep.) many of which were late-stage, raises the question of whether or not early alteration phases such as clay minerals, or ferric amphiboles would be preserved.

We are investigating the solubility of Pt in brine and supercritical fluid at temperatures of 600 – 900 °C and pressures of 1 – 2 kbar using cold seal bombs under conditions of simultaneously controlled pH, *f*O<sub>2</sub>, and salinity. Solubility measurements were obtained by analyzing quenched fluids both within sealed Pt capsules and within quartz as primary and secondary fluid inclusions. Pt capsules were loaded with salt (KCl) and deionized water (to obtain a specific KCl

molality at run conditions), pH buffer (andalusite-orthoclase-quartz), and electrolytically-cleaned Brazilian quartz chips. The loaded capsules were then welded shut with an arc welder. Capsules were weighed, heated to 110°C, and reweighed to check the integrity of the weld. The capsules were then placed in Rene-41 cold seal bombs with Ni filler rods. It was confirmed that the bomb and filler rod composition maintained  $fO_2$  at the Ni-NiO buffer for the duration of the experiments. Ni diffusion into the Pt capsule wall was examined by electron microprobe and did not penetrate more than 5  $\mu$ m into the outer capsule wall, therefore, measured solubilities are for Pt and not Pt-Ni alloy. Cold-seal bombs were pre-pressurized (with water) to run conditions and heated in clam-shell furnaces, while pressure was bled off and kept constant during heating. The thermal gradient over the entire length of the Pt capsules was 3°- 4°C. An internal thermocouple was used to monitor T at the hottest end of the capsules. After 100 hrs, which was deemed sufficient time for Pt metal to equilibrate with the capsule solution, the cold seal vessel was quenched rapidly to approximately 150°C below run conditions. This transition caused the quartz chips to fracture, in part due to thermal contraction, and/or in part due to the  $\alpha/\beta$  quartz transition. After fracturing, the capsules were returned to run conditions and allowed to re-equilibrate for another ~87 hours, which was deemed to be sufficient time for the fractures to heal. The purpose of this step was to ensure that the fluid inclusions were formed after equilibrium was reached. It was assumed that the readjustment in temperature after fracturing did not affect Pt solubility dramatically and that equilibrium would be reached again quickly. After full experimental duration (8 days = ~187 hrs), the cold seal bombs were quenched rapidly (1-1.5 min.) to room temperature using a cold water aerosol quench. The capsules were removed, reweighed to check for leakage, and cleaned in a 70 wt% Optima™ grade HNO<sub>3</sub> bath for 10 minutes, followed by a deionized water bath for 20 minutes. Capsules were immersed in 5.0 mL of deionized water in teflon vials and punctured to allow escape of the capsule fluid and dissolution of salt formed during the quench. The resulting volume of solution was acidified with 1 wt% Optima™ grade HNO<sub>3</sub> solution, filtered through a 0.45  $\mu$ m nylon filter and analyzed by ICP-MS. Routine detection limit for the analysis of Pt by this method was 10 ppt, and samples were analyzed with at least 5 repetitions per sample. Examination of the inner wall of the capsules after fluid was sampled did not reveal any quench phases, aside from amorphous silica globules which coated the entire inside wall. Run

products were examined by X-ray diffraction which confirmed that the pH buffer assemblage was present and that no new phases had formed.

From one of two experiments completed, the quartz chips within the capsules were removed, cleaned in DIW, and crushed in an agate mortar under 5mL of 1 wt% Optima™ grade HNO<sub>3</sub> solution. The resulting solution was analyzed by ICP-MS and concentrations of K and Pt were back-calculated (based on dilutions and known KCl molality) to determine Pt concentration in the trapped fluid volume. This step allowed us to examine the concentration of Pt in solutions trapped within the quartz as fluid inclusions, and provided a more accurate and absolute constraint on Pt solubility for comparison to the capsule fluids analyzed separately by ICP-MS. Measured solubilities from the fluid inclusions and capsule fluid differed by approximately 15%, with the lower value obtained from the fluid inclusions. For similar experiments at these experimental run conditions, microthermometry using a Linkam THMS-600 heating-cooling fluid inclusion stage and TMS-94 controller determined pressure-corrected trapping temperatures within 6.3°C of the set run temperature confirming that fluid inclusions are trapped at experimental run conditions.

Preliminary results have been collected for Pt solubility at 600°C/1kBar in a 50.4 wt% KCl solution and at 700°C/1.5 kBar in a 20wt% KCl solution. In these two experiments, Pt solubilities were on the order of 10<sup>3</sup> and 10<sup>2</sup> ppb respectively. Lower solubility was demonstrated in the higher temperature, lower salinity fluid. Log  $fO_2$  values calculated for the Ni-NiO buffer were -19.1 and -16.2 respectively for the 600 and 700°C runs. The molalities of free Cl<sup>-</sup> and pH values were calculated to be 0.042 m and 4.9 respectively in the 20 wt% KCl solution and 0.062 m and 4.6 in the 50 wt% KCl solution. These values were calculated using the EQBRM computer code (Anderson and Crerar, 1993) with equilibrium coefficients calculated from the SUPCRT (Dslp98.dat) database (Johnson et al., 1992). Measured Pt solubilities are comparable to those obtained for Os and Pd by Xiong and Wood (2000) at slightly lower temperatures, much lower salinities, and comparable to higher  $fO_2$ .

These results further demonstrate the counteractive effects of changing thermochemical conditions on PGE solubility. With increasing temperature above 600°C, free Cl<sup>-</sup> concentration decreases substantially and in general is very low (< 0.1 molal), suggesting that KCl<sup>0</sup><sub>(aq)</sub> is the dominant chloride species. Therefore, the observed increase in Pt solubility is more likely a result of

the depression in pH due to decreasing temperature and increasing salinity, rather than from changes in the availability of free Cl<sup>-</sup>. Alternately, the effects of changing salinity on Pt solubility may be equally important at these higher temperatures because of the expansion of the two-phase field in the H<sub>2</sub>O-KCl system. Based on theoretical predictions suggest that at very high temperatures (>1000 °C) the solubility of the PGE is several orders of magnitude lower in saline vapour than in the equivalent, more saline liquid phase at lower temperature (Wood, 1987). This may be another explanation for the increase in solubility with increasing salinity and decreasing temperature in this study. The fluid in the lower temperature run would have been present as a brine, whereas the higher temperature fluid would have been a low density vapour. This was confirmed for both experiments by examining the phase changes in fluid inclusions trapped within the quartz chips recovered from the capsules. More detailed study will accurately and thoroughly determine in detail the sensitivity of Pt solubility to these changing parameters at high T and salinity.

Based on the solubility obtained from these preliminary experiments and very conservative estimates of the fluid-rock ratios (~0.5) involved in the alteration of PGE-bearing rock types in the Merensky Reef and Picket Pin deposits, at least 20% of the total PGE contained in these deposits may have been carried in solution in early deuteric brines under conditions of P and T similar to those of our experiments.. Less conservative estimates of fluid-rock ratios allow all of the PGE to be transported or redistributed by these brines. The absence of low pH, high fO<sub>2</sub> alteration assemblages in the PGE-bearing horizons may result from overprinting of such early assemblages by successive pulses of later fluid activity.

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