Solubility of Pt in sulphide mattes: Implications for the genesis of PGE-rich horizons in layered intrusions

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Received 15 October 2008; accepted in revised form 23 June 2009; available online 19 July 2009

Abstract

The partitioning of Pt in sulphide melt (matte) has been studied as a function of fS_2 and fO_2 at 1200 and 1300 °C. The results show that the solubility of Pt in mattes increases strongly with increasing fS_2 and decreases weakly with increasing fO_2 . The increase in Pt solubility with increasing fS_2 is attributed to Pt dissolving in the melt as a sulphide species and the weak inverse dependence of Pt solubility on fO_2 to the diluting effect of increasing O in the melt at high fO_2 . These results, coupled with measurements of Pt solubility in silicate melts taken from the literature, allow the calculation of Pt matte/silicate-melt partition coefficients ($D_{Pt}^{matte-sil}$) for a range of conditions pertinent to the formation of Pt-rich horizons in layered intrusions. The calculated values range between 10^7 and 10^{11} , depending on fO_2 and fS_2 , several orders of magnitude higher than previously published values. Our preferred value for $D_{Pt}^{matte-sil}$ for conditions appropriate to the Merensky Reef is 10^7 and for the Stillwater Pt-rich horizon 10^8 . The new results are consistent with the magmatic hypothesis for Pt-rich horizons in layered intrusions.

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1. INTRODUCTION

Platinum Group Elements (Os, Ir, Ru, Pt, Pd and Rh – the PGE) have a high affinity for metallic and sulphide phases and as a consequence are defined as being both chalcophile and highly siderophile elements. The highly siderophile characteristics of Pt are well accepted, with measured distribution coefficients ($D_{Pt}^{metal-sil}$) as high as 10^{12} for the partitioning of Pt between metal and silicate melt. However, the extent to which Pt is chalcophile remains controversial, with measured partitioning coefficients for Pt between sulphide melt (here referred to as matte) and silicate melt ($D_{Pt}^{matte-sil}$) ranging between 10^3 and 10^9 . Many authors including Helz and Rait (1988), Peach et al. (1990, 1994), Stone et al. (1990), Fleet et al. (1991, 1996),

Bezmen et al. (1994), Crocket et al. (1997), and Fleet et al. (1999) accept values towards the lower end of this range (10^3 – 10^4). However, others (e.g., Bezmen et al., 1991; Pruseth and Palme, 2004) have calculated $D_{Pt}^{matte-sil}$ that are several orders of magnitude higher than these previous values (Table 1).

The controversy regarding the extent to which Pt is chalcophile affects whether the so-called “*R*-factor” model can explain PGE enrichment in magmatic sulphide deposits (e.g., Campbell and Naldrett, 1979). If $D_{Pt}^{matte-sil}$ is very large, the high-temperature equilibration between a matte and a silicate melt will inexorably lead to the matte being enriched in Pt when compared to the silicate melt. Furthermore, the enrichment would not only be a function of the high $D_{Pt}^{matte-sil}$ but, due to mass balance considerations, would also be constrained by the mass ratio of the silicate liquid to sulphide liquid, *R*. The *R*-factor model, which was initially proposed by Campbell and Naldrett (1979), has been used to explain the high PGE enrichments observed in horizons found in a number of mafic layered intrusions such as the Merensky Reef, Stillwater complex, etc. (e.g., Keays

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Table 1

Summary of some of the different matte/silicate and metal silicate partition coefficients for Pt and Pd available in the literature.

Authors	Temperature (°C)	Pressure (bars)	$-\log fS_2$	$-\log fO_2$	$D_{\text{Pt}}^{\text{matte-sil}}$	$D_{\text{Pd}}^{\text{matte-sil}}$
Bezmen et al. (1991)	1200–1350	100–4000	0.1–3.7	9.9–12.4	>106	–
Bezmen et al. (1994)	1200–1300	1000–4000	0.3–4	9.9–12	–	5.5×10^4
Crocket et al. (1997)	1250	1	0.9	8.6	1.65×10^4	2.8×10^4
Fleet et al. (1991)	1300	1	–	CCO ^a –WM ^b	2.00×10^4	2.00×10^4
Fleet et al. (1996)	1250	1	0.9–1.0	8.5–8.6	1.50×10^4	–
Fleet et al. (1999)	1300	1	0.2–2.3	11.4–12	1.30×10^4	2.50×10^4
Helz and Rait (1988)	–	–	–	–	3.6×10^4	2.50×10^4
Peach et al. (1990)	1260	1	–	QFM ^{–0.5}	1×10^3	2.30×10^4
Peach et al. (1994)	1450	8000	2.3–1	~QFM ^{2.5}	–	3.4×10^4
Pruseth and Palme (2004)	1100–1300	1	0–6	QFM ^c (assumed)	>10 ⁹	–
Stone et al. (1990)	1200	1	0.9	9.2	9.1×10^3	8.80×10^4

^a C–CO–CO₂ oxygen fugacity buffer.^b Wustite–magnetite oxygen fugacity buffer.^c Quartz–fayalite–magnetite oxygen fugacity buffer. Taken from Mallmann and O'Neill (2007).

and Campbell, 1981; Campbell et al., 1983; Campbell and Barnes, 1984; Barnes and Naldrett, 1985; Naldrett et al., 1987; Barnes and Campbell, 1988; Godel et al., 2007). However, the *R*-factor model was almost immediately criticized, because until recently, $D_{\text{Pt}}^{\text{matte-sil}}$ available in the literature (e.g., Helz and Rait, 1988; Peach et al., 1990, 1994; Stone et al., 1990; Fleet et al., 1991, 1996, 1999; Bezmen et al., 1994; Crocket et al., 1997) were lower than required by the model to explain the level of PGE enrichment in sulphides observed in many magmatic PGE deposits. Fleet et al. (1999) for example, argued that the low $D_{\text{PGE}}^{\text{matte-sil}}$ values measured in their experiments, and also those measured by Peach et al. (1994), were not consistent with the enrichments observed in the reef deposits of the Bushveld and Stillwater complexes. Fleet et al. (1999) instead proposed that the discrepancy between measured $D_{\text{PGE}}^{\text{matte-sil}}$ and the empirically determined $D_{\text{PGE}}^{\text{matte-sil}}$ argued in favor of an “upward” migrating fluid as the source of PGE enrichment. This view was reiterated by Mathez (1995) who pointed out that because PGE enrichments in mafic layered intrusions are often associated with textural indicators for extensive metasomatism, “it may be taken as evidence that the PGE were enriched by a metasomatic process”, a view that found support in a number of subsequent studies (Ballhaus and Stumpfl, 1985, 1986; Boudreau and McCallum, 1992; Boudreau and Meurer, 1999; Meurer et al., 1997; Meurer and Boudreau, 1998). However, Wood (1987) pointed out that even though PGE may be transported in Cl-rich brine fluids, as suggested for instance by Boudreau and McCallum (1992) and Boudreau and Meurer (1999), Cu, Ni and Fe should be more enriched by hydrothermal fluids than the PGE by “several factors of tens”, which is not observed in the PGE-rich reefs of the Stillwater and Bushveld Complexes. Moreover, PGE abundances in hydrothermal sulphides are typically very low as shown in a recent study by Luguet et al. (2004), further reinforcing the likelihood that PGE cannot be strongly enriched by hydrothermal fluids. A more detailed discussion on the pros and cons of the “upward” migrating fluid model may be found on Barnes and Campbell (1988).

The discrepancies between estimates for $D_{\text{Pt}}^{\text{matte-sil}}$ are at the core of the debate between the “upper”, those who

advocate a hydrothermal origin of PGE-rich reefs, and the “downers”, who favor a magmatic origin. The direct experimental determination of Pt (or PGE) matte/silicate-melt partition coefficients ($D_{\text{Pt}}^{\text{matte-sil}}$) is difficult (e.g., O'Neill et al., 1995). Although there are numerous experimental data on the partitioning of Pt between mattes and silicate melts (Bezmen et al., 1991, 1994; Crocket et al., 1997; Fleet and Stone, 1991; Fleet et al., 1996, 1999; Peach et al., 1990, 1994; Stone et al., 1990), early experimental attempts to measure $D_{\text{Pt}}^{\text{matte-sil}}$ directly are now thought to have been compromised by the presence of “nanonuggets” in run products. Nanonuggets consist of sub-micron particles of Pt metal and/or Pt-rich sulphides globules that remain suspended in the silicate melt, resulting in an overestimate of the Pt content in the quenched glass, which lead to $D_{\text{Pt}}^{\text{matte-sil}}$ that may be orders of magnitude too low (e.g., O'Neill et al., 1995; Ertel et al., 1999, 2008). The advent of laser-ablation ICP–MS as a microanalytical method suitable for determining PGEs in experimental run products has confirmed the ubiquity of the nanonugget problem.

As pointed out by O'Neill et al. (1995), the customary experimental tactic of performing “reversal” experiments to test for equilibrium does not address the nanonugget problem. The “reversal” tactic was introduced into experimental petrology specifically to guard against erroneous results that often arise in silicate systems due to sluggish nucleation and growth, and is irrelevant to sulphide/silicate melt partitioning experiments where nucleation is not an issue and diffusion kinetics are rapid. Instead, the different problems of PGE partitioning experiments demand that other criteria be used to assess equilibrium, such as demonstration of a smooth response to variations in the physical variables to which partitioning is expected to be sensitive, particularly oxygen fugacity (fO_2) and sulphur fugacity (fS_2). At present, no studies that have tried to measure PGE matte/silicate partitioning directly have attempted the appropriate tests for equilibrium.

Unless special experimental techniques can be found to eliminate the nanonugget problem (e.g., Brenan, 2008), the PGE partitioning needed to discriminate between models must be obtained indirectly, by performing experiments under conditions where nanonuggets do not pose an over-

whelming obstacle to measuring equilibrium relations, and then combining the results in a thermodynamic model to calculate the desired quantities, such as $D_{\text{PGE}}^{\text{matte-sil}}$. This approach also has the advantage that the sensitivity of $D_{\text{Pt}}^{\text{matte-sil}}$ to petrologically important variables is also obtained.

Here we report experiments in which the solubility of Pt in mattes was investigated as a function of $f\text{O}_2$, $f\text{S}_2$ and temperature. The results may be combined with solubility data for Pt in silicate melts at 1 bar of Ertel et al. (1999), Borisov and Palme (1997, 2000), and Fortenfant et al. (2003), and the activity–composition relationships of Pt–Fe alloys (Gudmundsson and Holloway, 1993), to calculate $D_{\text{Pt}}^{\text{matte-sil}}$ over a range of conditions that are pertinent to the upper mantle and crust. We shall show that the very high values of $D_{\text{PGE}}^{\text{matte-sil}}$ calculated by this method require that the high-temperature equilibrium between a matte and a silicate melt will lead to the matte being greatly enriched in Pt.

2. EXPERIMENTAL METHODS

Three sets of experiments were carried out to evaluate the effects of T , $f\text{O}_2$ and $f\text{S}_2$ separately on the solubility of Pt in mattes. For each set of experiments two thermodynamic variables were kept constant while the third was varied. The experimental set-up was the same for all experiments. Each experimental charge consisted of troilite (Fe/S atomic = 1) powder of 99.99% purity placed inside an open capsule made from pure SiO_2 glass, and contained a loop of Pt wire. The crucibles were suspended in a vertical muffle tube furnace equipped for gas mixing, in which both $f\text{O}_2$ and $f\text{S}_2$ were controlled independently using CO_2 – CO – SO_2 gas mixtures. The gas flows were measured using Tylan F2800 mass flow controllers. Two controllers were available for each gas: for CO and CO_2 the controller had ranges between 0–10 and 0–200 SCCM (standard cubic centimeters per minute) and 0–10 and 0–100 SCCM for SO_2 . The $f\text{O}_2$ and $f\text{S}_2$ for each run were calculated using the thermodynamic data for gas species in the NIST-JANAF tables (Chase, 1998) according to O'Neill and Mavrogenes (2002). Temperature was held constant to $\pm 5^\circ$ for the duration of each run using a central Pt–Rh thermocouple external to the muffle tube. Run times of 96, 72 and 24 h were used to ensure equilibrium between the Pt metal and the mattes in the runs performed at 1200, 1300 and 1400 $^\circ\text{C}$, respectively. Equilibrium was subsequently tested by analysing Fe and Pt in line profiles through sections of the Pt wire and the Pt content of the matte at different run times (between 1 and 96 h) and constant $f\text{S}_2$ (0.001 bars), $f\text{O}_2$ (10^{-11} bars) and temperature (1200 $^\circ\text{C}$). Profiles of the metal wire at the end of each run (Fig. 1A), showed that the wire is strongly zoned at run times of less than 4 h, and homogeneous after 24 h run time. The activity of Pt is higher in the beginning of a run because Fe has not diffused completely into the metal wire. This led to the zonation of the metal wire with respect to Pt (Fig. 1A), and higher concentrations of Pt in the matte (Fig. 1B) at 1 and 4 h of run time. However, after 24 h of run time, the metal wire reaches its equilibrium Fe and Pt contents, (Fig. 1A), and displays a con-

Fig. 1. (A) Profile of the Pt content of the metal phase for different run times. Curves represent five point moving averages derived from 30 to 50 EMP point analyses for each profile. (B) Pt content in matte at different run times. Time series carried out at constant $f\text{S}_2$ (0.001 bars), $f\text{O}_2$ (10^{-11} bars) and temperature (1200 $^\circ\text{C}$).

stant Pt solubility in the matte over time (Fig. 1B). At the end of each run the charges were quenched by dropping them into a beaker of water at room temperature. The experimental products were then recovered, mounted in epoxy resin and polished for analysis.

3. ANALYTICAL METHODS

3.1. Petrographical description

Unlike many silicate liquids, mattes do not quench to a glass but to a texturally complex mass of crystalline sulphide, metals and oxides, depending on the composition, requiring special care in determining the composition of the original matte.

Fig. 2B is a Pt X-ray map of a typical quenched experimental run, which shows that a Pt metal phase exsolves from the matte during quenching. In addition, a depletion halo, $\sim 40 \mu\text{m}$ wide, formed around the original Pt-rich

Fig. 2. (A) Pt X-ray map of run PtO11 for Pt. The original Pt metal (in the top center) is surrounded by a depletion halo (1) where no Pt is observed due to Pt diffusion into the Pt wire during quenching. The sulphide phase includes quench nuggets of PtFe metal (2) which exsolved from the matte during quenching. (B) Backscatter electron image of run PtS1. This is a typical run product where nuggets of PtFe are rosette shaped indicating they are a product of quenching.

metal upon quenching. A closer look at the PtFe quench nuggets shows typical quench textures (Fig. 2B), which indicates that these nuggets are the result of exsolution of dissolved Pt in the matte. The scale of the quench textures also varies depending on which part of the charge is considered. The quench nuggets tend to be larger near the center of the crucible because quenching is slower. Moreover, the shape of the quench nuggets is dependent on the f_{S_2} of the run, which controls the speciation of Pt in the matte. Any measurement of the Pt content of the matte has to include these Pt-rich quench nuggets, as they represent Pt that was dissolved in the matte prior to quenching. This requires the experiments to be performed at a scale sufficiently large to produce areas of quenched sulphide suitable for representative analyses.

3.2. Electron microprobe analysis – major elements

Both sulphide and metal phases were analysed using the CAMECA-SX100 Electron Microprobe, in wavelength dispersive mode (WDS), with 15 kV acceleration voltage and 20 nA beam current. The alloys were analysed using line profiles across the wire, and the sulphides as area scans in $300 \mu\text{m} \times 300 \mu\text{m}$ grids. Standard calibrations were carried out using $\text{Pt}_{0.7}\text{Rh}_{0.3}$ metal for Pt and pure troilite for Fe and S. Oxygen was analysed using the CAMECA-SX100 EMPA, in WDS mode. Calibrations for O were conducted on rutile (TiO_2), chromite and quartz using the PC0 monolayer pseudocrystal, following the methodology described in detail in Fonseca et al. (2008).

3.3. Laser ablation mass spectrometry (LA-ICP-MS) – trace elements

LA-ICP-MS was used for trace element analysis in the sulphide phase, following the procedure described by [Fonseca et al. \(2007\)](#) with ^{57}Fe as the internal standard. The standard used was the CANMET727T2 synthetic PGE and Au bearing FeS from the Memorial University of Newfoundland. The spot size for all analyses was 112 μm , the laser repetition rate was 5 Hz, and the laser pulse energy was 120 mJ with $\sim 75\%$ energy loss, resulting in a fluence of $\sim 265 \text{ J cm}^{-2}$. The Pt isotopes ^{194}Pt , ^{195}Pt and ^{196}Pt were analysed, which produced results in good agreement with each other, showing that there were no significant interferences from other isotopes or molecular compounds. Platinum metal has a very low vapor pressure when compared to mattes. It is therefore possible that, during ablation of the sample, Pt alloys may not ablate at the same rate as the matte matrix, resulting in lower measured Pt concentrations. This possibility was tested by measuring Pt contents in matte over a range of laser pulse energies, between $\sim 25 \text{ mJ}$ (100 mJ laser output, filtered by 25% optical mirror), and 160 mJ (no transmission loss). The measured Pt concentrations in mattes were constant over the range of laser pulse energies used, indicating that Pt alloys are not fractionated relative to Fe and S in the matte during ablation.

4. THEORETICAL BACKGROUND

The solubility of Pt in mattes requires an understanding of the effects of several competing variables, the most important of which are likely to be temperature, $f\text{S}_2$ and $f\text{O}_2$. Platinum could dissolve in a matte as oxide, sulphide and metal species, with solution reactions taking the following form:

where x is the effective valence state of Pt in the matte. The common valence state of Pt in silicate melts in the oxygen fugacity regime of the terrestrial upper mantle appears to be Pt^{2+} , but Pt^{4+} occurs at higher $f\text{O}_2$ ([O'Neill et al., 1995](#); [Ertel et al., 1999](#)), and is the common higher oxidation state of Pt in many chemical compounds. Any change in valence must profoundly affect the solubility of Pt in mattes, and experiments that do not address this most important aspect of PGE chemistry cannot be extrapolated to natural systems reliably.

5. RESULTS

5.1. Activities of Fe and Pt in the metal phase

The major element composition of mattes and alloys, as well as the experimental run conditions, are presented in [Table 2](#). The results show that the Pt-rich metal phase in

equilibrium with the sulphide-rich matte in the experimental runs display varying concentrations of Fe, which changes the activity of Pt ($a_{\text{Pt}}^{\text{metal}}$) in the system Fe–Pt–S–O. The Pt–Fe binary shows a very strong negative deviation from Henry's law ([Gudmundsson and Holloway, 1993](#); [Okamoto, 2002](#)). Since the majority of the (Pt,Fe) alloys obtained in the experimental runs in this study fell within the face-centered cubic continuous solid solution (γ -phase) field in the FePt phase diagram, the activities of Pt and Fe in the metal were calculated from the equations of [Gudmundsson and Holloway \(1993\)](#):

$$\log \gamma_{\text{Fe}} = (1 - X_{\text{Fe}})^2 [B + C(4X_{\text{Fe}} - 1)] \quad (4)$$

$$\log \gamma_{\text{Pt}} = X_{\text{Fe}}^2 [B + C(4X_{\text{Fe}} - 3)] \quad (5)$$

where γ_{Pt} and γ_{Fe} are the activity coefficients of Pt and Fe, respectively, X_{Fe} is the mole fraction of Fe in the metal, and B and C are temperature-dependent constants. [Gudmundsson and Holloway \(1993\)](#) only determined B and C for the temperatures of 1300 and 1400 °C. Since our experimental runs were also conducted at 1200 °C, the values for these constants were linearly extrapolated to lower temperatures following [Pruseth and Palme \(2004\)](#), yielding:

$$B = 0.0062T - 12.302 \quad (6)$$

$$C = 0.0017T - 2.565 \quad (7)$$

A listing of all activity coefficients and activities of Pt and Fe is provided in [Table 3](#). Measured concentrations of Pt in the matte may be normalised to unit activity of Pt in the alloy (i.e., $a_{\text{Pt}}^{\text{metal}} = 1$) using $[\text{Pt}]_{\text{matte}}^{\text{a-norm}} = [\text{Pt}]_{\text{matte}} / a_{\text{Pt}}^{\text{metal}} [\text{Pt}]$ ([Table 3](#)).

5.2. The effect of $f\text{S}_2$

The effect of $f\text{S}_2$ on the solubility of Pt in mattes was investigated through experiments that were carried out at a constant $f\text{O}_2$ of $10^{-13.0}$ bar ($\sim \text{QFM-5}$) at 1200 °C, and $10^{-11.3}$ bar ($\sim \text{QFM-4}$) at 1300 °C, and over a range of $f\text{S}_2$ between $10^{-4.9}$ and $10^{-1.3}$ bar. The Pt concentrations in matte increase with increasing $f\text{S}_2$ ([Fig. 3A](#)). The normalised solubility of Pt in the matte ($[\text{Pt}]_{\text{matte}}^{\text{a-norm}}$) shows the same behaviour as the raw solubility data, in that Pt concentrations increase with increasing $f\text{S}_2$ except at $f\text{S}_2 > 10^4$. The slope of 0.47 given by an empirical fit to the activity normalised data in [Fig. 3A](#) suggests a valency of Pt^{2+} . At these $f\text{S}_2$, $[\text{Pt}]_{\text{matte}}^{\text{a-norm}}$ increases whereas the raw solubility decreases. Matte composition also changed with $f\text{S}_2$, from Fe/S (atomic fraction) ~ 0.9 at high $f\text{S}_2$, to ~ 1.2 at low $f\text{S}_2$ ([Fig. 3B](#)).

5.3. The effect of $f\text{O}_2$

[Kress \(1997, 2007\)](#), [Larocque et al. \(2000\)](#), [Fonseca et al. \(2008\)](#), and [Moretti and Baker \(2008\)](#) investigated the effects of $f\text{O}_2$ and $f\text{S}_2$ in the system Fe–S–O and observed that a considerable amount of oxygen ($\sim 7 \text{ wt\% O}$) was dissolved in the matte at the $f\text{O}_2$ defined by the quartz–fayalite–magnetite buffer (QFM). If O dissolves in the matte, the possible effect of $f\text{O}_2$ needs to be investigated in view of reaction 2. [Andrews and Brenan \(2002\)](#) studied the effect of $f\text{O}_2$ as

Table 2
Experimental conditions and major and trace element concentrations.

Run	Run conditions					Composition of the sulphide matte					$\chi_{\text{Pt}}^{\text{metal}}$
	$-\log f_{\text{S}_2}$	$-\log f_{\text{O}_2}$	Pt/FeS ^a	T (°C)	Run time (h)	Fe (wt%)	S (wt%)	O (wt%)	Pt (ppm)	Total (wt%)	
Pt1h	2.94	10.9	0.2	1200	1	63.9 ± 0.3	33.2 ± 0.1	0.8 ± 0.2	11204 ± 1512	99.0	0.65
Pt4h	2.94	10.9	0.2	1200	4	62.3 ± 0.2	36.4 ± 0.3	1.5 ± 0.3	17103 ± 3210	101.9	0.83
Pt24h	2.94	10.9	0.2	1200	24	59.1 ± 0.4	36.7 ± 0.8	1.6 ± 0.1	11488 ± 948	98.6	0.53
Pt48h	2.94	10.9	0.2	1200	48	58.2 ± 0.4	39.8 ± 0.1	2.4 ± 0.4	6146 ± 675	101.0	0.52
Pt96h/PtO11	2.94	10.9	0.2	1200	96	64.1 ± 0.1	33 ± 0.4	3.5 ± 0.2	6234 ± 1567	101.2	0.54
PtO9 ^b	3.05	9.0	0.2	1200	96	52.8 ± 0.5	6.1 ± 1.1	29.8 ± 0.8	3 ± 2	88.7	0.88
PtO10	2.94	10.3	0.2	1200	96	64.8 ± 0.1	27.4 ± 0.2	6.91 ± 0.5	3189 ± 122	99.4	0.52
PtO11/Pt96h	2.94	10.9	0.2	1200	96	64.1 ± 0.2	33.0 ± 0.3	3.46 ± 0.4	3785 ± 39	100.9	0.51
PtO12	2.24	11.8	0.2	1200	96	64 ± 0.1	32.6 ± 0.4	2.1 ± 0.1	6898 ± 916	99.4	0.52
PtO13/PtS3	2.94	12.9	0.2	1200	96	64.6 ± 0.5	34.2 ± 0.2	0.5 ± 0.1	6112 ± 1121	99.9	0.49
PtO15	3.05	14.9	0.2	1200	96	60.9 ± 0.6	35.2 ± 0.2	bdlc	25354 ± 375	98.6	0.5
PtS1/PtH2	1.31	11.8	0.2	1200	96	58.5 ± 0.4	35.1 ± 0.6	0.2 ± 0.1	62927 ± 1939	100.1	0.63
PtS2	2.21	12.9	0.2	1200	96	62.9 ± 0.1	34.9 ± 0.5	0.2 ± 0.1	26525 ± 715	100.7	0.6
PtS3/PtO13	2.94	12.9	0.2	1200	96	64.6 ± 0.2	34.2 ± 0.4	0.3 ± 0.1	6112 ± 1121	99.7	0.49
PtS4	3.96	12.8	0.2	1200	96	66.1 ± 0.4	33.6 ± 0.1	0.4 ± 0.1	1665 ± 273	100.3	0.42
PtS5	4.96	13.1	0.2	1200	96	66.0 ± 0.9	32.5 ± 0.1	1.5 ± 0.3	816 ± 259	100.0	0.33
PtH1	2.21	13.1	0.1	1200	96	64.1 ± 1.1	35.2 ± 0.4	bdl	7700 ± 529	100.1	0.51
PtH2	1.31	11.8	0.2	1200	96	58.5 ± 0.5	35.1 ± 0.3	bdl	62967 ± 1263	99.9	0.7
PtH3	2.21	12.9	1.0	1200	96	57.9 ± 0.1	34.6 ± 0.5	bdl	62927 ± 1939	98.8	0.8
Pt#1	1.61	11.3	0.2	1300	72	58.4 ± 0.1	34.8 ± 0.1	0.2 ± 0.1	55622 ± 2491	99.0	0.62
Pt#2	1.81	11.3	0.2	1300	72	60.2 ± 0.2	33.9 ± 0.1	0.3 ± 0.2	45000 ± 3741	98.9	0.6
Pt#3	2.10	11.3	0.2	1300	72	61.4 ± 0.5	34.1 ± 0.3	0.9 ± 0.3	30650 ± 4030	99.5	0.57
Pt#4	2.48	11.4	0.2	1300	72	63.5 ± 0.1	33.6 ± 0.1	0.6 ± 0.1	17807 ± 2167	99.5	0.54
Pt#5	2.84	11.4	0.2	1300	72	64.4 ± 0.1	33.1 ± 0.2	1.5 ± 0.2	8500 ± 674	99.9	0.5
Pt#6	3.15	11.2	0.2	1300	72	64.5 ± 0.3	31.7 ± 0.6	2.0 ± 0.2	6573 ± 386	98.9	0.48
Pt#7	3.64	11.4	0.2	1300	72	63.5 ± 0.8	33.8 ± 0.2	2.1 ± 0.5	6027 ± 661	100.0	0.5
Pt#8	3.05	13.7	0.2	1300	72	63.7 ± 0.1	34.4 ± 0.8	0.5 ± 0.3	12210 ± 679	99.8	0.5
Pt#9	2.88	12.7	0.2	1300	72	63.3 ± 0.4	34.2 ± 0.3	1.1 ± 0.2	13408 ± 2250	99.9	0.49
Pt#10	2.83	10.3	0.2	1300	72	64.5 ± 0.5	30.5 ± 0.1	4.0 ± 0.7	7474 ± 485	99.7	0.52
Pt#11 ^c	2.94	9.7	0.2	1300	72	52.9 ± 1.1	5.6 ± 0.9	28.6 ± 0.5	97 ± 2	87.1	0.54
Pt#12	1.58	10.3	0.2	1400	24	59.4 ± 0.7	33.9 ± 0.2	1.1 ± 0.3	41524 ± 6630	98.6	0.59
Pt#13	3.88	10.3	0.2	1400	24	61.7 ± 0.2	33.4 ± 0.3	2.8 ± 0.6	27437 ± 3149	100.6	0.57
Pt#14	1.61	11.3	0.8	1300	72	59.2 ± 0.1	34.5 ± 0.1	bdl	61227 ± 1564	99.8	0.62
Pt#15	1.61	11.3	1.0	1300	72	58.8 ± 0.0	34.0 ± 0.5	bdl	70950 ± 1294	99.9	0.62

^a Initial Pt/FeS wt% of the experimental charge.

^b Reacted extensively with the SiO₂ capsule with 11.1 wt% Si dissolved in the matte.

^c Reacted extensively with the SiO₂ capsule with 10.9 wt% Si dissolved in the matte.

Table 3

Calculate activity coefficients for Pt in the metal phase and correspondent partition coefficients.

Run	$\gamma_{\text{Pt}}^{\text{metal}^a}$	$a_{\text{Pt}}^{\text{metal}}$	$[\text{Pt}]_{\text{matte}}^{\text{a-norm}} \text{ (wt\%)}^b$	$[\text{Pt}]_{\text{sil-melt}} \text{ (ppb)}^c$	$D_{\text{Pt}}^{\text{metal/matte}}$	$D_{\text{Pt}}^{\text{metal/sil}}$	$D_{\text{Pt}}^{\text{matte/sil}}$
Pt1h	0.327	0.214	5.2	0.0274	77	3.65×10^{10}	4.75×10^8
Pt4h	0.79	0.658	2.6	0.0274	55	3.65×10^{10}	6.63×10^8
Pt24h	0.111	0.058	19.7	0.0274	69	3.65×10^{10}	5.28×10^8
Pt48h	0.1	0.052	11.9	0.0274	127	3.65×10^{10}	2.87×10^8
Pt96h/PtO11	0.12	0.064	9.7	0.0274	130	3.65×10^{10}	2.80×10^8
PtO10	0.102	0.053	6	0.07901	251	1.27×10^{10}	5.05×10^8
PtO11/Pt96h	0.094	0.048	7.9	0.0274	206	3.65×10^{10}	1.77×10^8
PtO12	0.104	0.054	12.8	0.00995	114	1.01×10^{11}	8.78×10^8
PtO13/PtS3	0.077	0.038	16	0.00268	128	3.74×10^{11}	2.92×10^9
PtO15	0.086	0.043	58.8	0.00025	32	4.00×10^{12}	1.30×10^{11}
PtS1/PtH2	0.283	0.179	35.2	0.00995	14	1.01×10^{11}	7.07×10^9
PtS2	0.216	0.13	20.5	0.0025	32	4.00×10^{11}	1.26×10^{10}
PtS3/PtO13	0.077	0.038	16	0.00268	128	3.74×10^{11}	2.92×10^9
PtS4	0.031	0.013	12.9	0.0025	437	4.00×10^{11}	9.17×10^8
PtS5	0.009	0.003	28.4	0.0025	792	4.00×10^{11}	5.05×10^8
PtH1	0.09	0.046	16.8	0.0025	104	4.00×10^{11}	3.87×10^9
PtH2	0.432	0.301	21	0.00995	14	1.01×10^{11}	7.07×10^9
PtH3	0.719	0.578	10.9	0.0025	15	4.00×10^{11}	2.71×10^{10}
Pt#1	0.28	0.172	32.3	0.02458	15	4.07×10^{10}	2.68×10^9
Pt#2	0.248	0.148	30.4	0.02458	18	4.07×10^{10}	2.20×10^9
Pt#3	0.193	0.109	28.1	0.02458	26	4.07×10^{10}	1.54×10^9
Pt#4	0.152	0.082	21.8	0.02458	45	4.07×10^{10}	9.01×10^8
Pt#5	0.109	0.055	15.6	0.02458	93	4.07×10^{10}	4.37×10^8
Pt#6	0.092	0.044	14.8	0.02458	118	4.07×10^{10}	3.44×10^8
Pt#7	0.106	0.053	11.4	0.02458	130	4.07×10^{10}	3.12×10^8
Pt#8	0.105	0.052	23.4	0.00157	64	6.37×10^{11}	9.99×10^9
Pt#9	0.093	0.045	29.8	0.00514	58	1.95×10^{11}	3.39×10^9
Pt#10	0.128	0.066	11.3	0.08234	107	1.21×10^{10}	1.14×10^8
Pt#12	0.268	0.158	26.3	0.0814	20	1.23×10^{10}	6.12×10^8
Pt#13	0.235	0.134	20.5	0.0814	30	1.23×10^{10}	4.08×10^8
Pt#14	0.29	0.179	34.1	0.02458	14	4.07×10^{10}	2.90×10^9
Pt#15	0.291	0.181	39.3	0.02458	12	4.07×10^{10}	3.34×10^9

^a Calculated from Eq. (5).^b Pt concentration in the matte normalised to unit activity – $[\text{Pt}]_{\text{matte}}/a_{\text{Pt}}^{\text{metal}}$.^c Calculated from Ertel et al. (1999) and corrected for temperature using Fortenfant et al. (2003).

well as $f(\text{S}_2)$ on the solubility of Ru in matte and found that increasing $f(\text{O}_2)$ decreased the solubility of Ru. They suggested that the observed negative correlation between Ru solubility and $f(\text{O}_2)$ shows that Ru oxide is not a species in the matte and that the addition of oxygen raises $\gamma_{\text{Ru}}^{\text{matte}}$. More recently, Fonseca et al. (2007) showed that Re solubility in sulphide-rich matte has no obvious dependence on $f(\text{O}_2)$, except at $f(\text{O}_2)$ larger than $\sim 10^{-10}$ bar where solubility decreases sharply due to the formation of an oxide-rich matte.

The influence of $f(\text{O}_2)$ on the solubility of Pt in mattes was investigated through a series of experiments that were carried out at a nearly constant $f(\text{S}_2)$ of $\sim 10^{-3.0}$ bar and over a range of $f(\text{O}_2)$, between $10^{-14.9}$ and $10^{-9.0}$ bar (QFM-6.6 and QFM-0.8) at 1200 °C and between $10^{-13.7}$ and $10^{-9.6}$ bar (QFM-6.4 and QFM-2.3), at 1300 °C. The concentration of Pt in matte showing no clear dependence on $f(\text{O}_2)$, except at $f(\text{O}_2) > 10^{-10}$ bar when solubility decreases sharply to less than 100 ppm (Fig. 4A), indicating that Pt does not dissolve as an oxide component as in reaction 2. The sharp decrease in Pt solubility in matte at $f(\text{O}_2) > 10^{-10}$ bar is probably due to the increasing amounts of oxygen dissolving into the matte at the expense of sul-

phur, decreasing the amount of sulphur in the matte available to react with Pt (reaction 1). The matte also gets more metallic as $f(\text{O}_2)$ decreases which is shown by the higher Fe/(S + O) of the matte a lower $f(\text{O}_2)$ (Fig. 4B).

5.4. The Pt–Fe–(S + O) pseudo-ternary

The concentration of Pt, in both metal and sulphide phases, can be plotted on the Fe–Pt–(S + O) pseudo-ternary diagram (Fig. 5). The results agree with the ternary plots of Pruseth and Palme (2004) at 1200 and 1300 °C. Majzlan et al. (2002) and Pruseth and Palme (2004) observed that there is a direct correlation between high Pt concentrations in the matte and Pt contents of the alloys in equilibrium with the matte, for runs carried out at variable $f(\text{S}_2)$ (Fig. 5). The chemographic trend shown in the close ups in Fig. 5 suggests that Pt might dissolve into the melt as PtS, a well known Pt-bearing phase, with a valence of Pt^{2+} , which is consistent with the good fit between the plotted data and the slope of the FeS–PtS binary seen in Fig. 3. The dissolution of Pt in the sulphide-rich matte as PtS is not surprising considering that the free energy of for-

Fig. 3. Pt concentrations in matte in equilibrium with Pt metal at different f_{S_2} and constant f_{O_2} at 1200 and 1300 °C. Pt concentrations were normalised to unit activity of Pt because these experiments had significant amounts of Fe in the metal phase, therefore $[Pt]_{matte}^{norm} = [Pt]_{matte}/a_{Pt}^{metal}$. Error bars (2σ standard error) in log plot smaller than symbols. (B) Fe/S (at%) as a function of f_{S_2} . Because the experimental system is an open one, matte composition changes over the range of f_{S_2} studied. Such a variation is demonstrated by the Fe/S (at%) of the matte, which approaches unity at high f_{S_2} .

mation of PtS, over the range of temperatures studied, is almost an order of magnitude lower than that of PtS₂, which is not a known natural phase (Barin, 1989).

In runs where oxygen fugacity was varied, no such correlation is observed, because Pt does not dissolve as an oxide component as in reaction 4. According to Raghavan (1988), three distinct alloys are stable at the temperature of 1200 °C, a γ phase which represents a continuous solid solution between Fe and Pt, and two ordered phases, FePt, and FePt₃, representing miscibility gaps. At 1300 °C, only γ and FePt₃ are present. All but one of the PtFe alloys analysed to date fall within or at the boundary of the γ field. No significant difference was found in Pt solubility measurements in matte, between 1200 and 1300 °C, showing that temperature is not an important factor over the range studied, and therefore will not be considered further.

5.5. Platinum solubility in mattes and $D_{Pt}^{matte/sil}$

Previous experimental measurements of Pt solubility in silicate melts were obtained from Fe-free anorthite-diopside

Fig. 4. (A) Pt concentrations in matte at different f_{O_2} , constant f_{S_2} and 1200–1300 °C. Note that there is a small negative dependence of Pt contents on f_{O_2} until at higher f_{O_2} when Pt solubility suddenly drops. Error bars (2σ standard error) smaller than symbols. (B) The metallic character of the matte (Fe/S + O) decreases with increasing f_{O_2} .

eutectic melts (Borisov and Palme, 1997; Ertel et al., 1999; Fortenfant et al., 2003). Moreover, as shown in Fig. 3B, matte composition, i.e., its molar Fe/S, changes as a function of f_{S_2} and f_{O_2} . It is therefore desirable to derive an expression that describes the partitioning of Pt between matte and silicate melt as a function of f_{S_2} and f_{O_2} , which is independent of the Fe content of the two phases. From the Fe–(S + O)–Pt ternary phase diagram (Fig. 5A and B), it was established that Pt should dissolve into the sulphide-rich matte as PtS according to the reaction:

for which the equilibrium is:

$$\frac{-\Delta G(8)}{RT} = \ln a_{PtS}^{matte} - \frac{1}{2} \ln f_{S_2} - \ln a_{Pt} \quad (9)$$

Because Pt dissolves in silicate melt at geologically relevant redox conditions as Pt²⁺ (Borisov and Palme, 1997; Ertel et al., 1999; Fortenfant et al., 2003):

$$\frac{-\Delta G(10)}{RT} = \ln a_{PtO}^{sil} - \frac{1}{2} \ln f_{O_2} - \ln a_{Pt} \quad (11)$$

Fig. 5. Compositions of the matte plotted on the Fe–Pt–(S + O) ternary at 1200 °C (A) and 1300 °C (B). Tie lines connect the equilibrium compositions of matte to the corresponding metal. Solid lines represent binary systems (e.g., FeS–PtS). In both cases, the more Pt-rich sulphides appear to follow a path along the FeS–PtS binary.

Subtracting Eq. (11) from Eq. (9) eliminates a_{Pt} , to give:

$$\ln a_{\text{PtO}}^{\text{sil}} - \ln a_{\text{PtS}}^{\text{matte}} = \frac{-\Delta G(10) + \Delta G(8)}{RT} + \frac{1}{2} \ln f_{\text{O}_2} + \frac{1}{2} \ln f_{\text{S}_2} = \ln \left(\frac{X_{\text{PtO}}^{\text{sil}} \gamma_{\text{PtO}}^{\text{sil}}}{X_{\text{PtS}}^{\text{matte}} \gamma_{\text{PtS}}^{\text{matte}}} \right) \quad (12)$$

The partition coefficient of Pt between matte and silicate melt is defined as:

$$D_{\text{Pt}}^{\text{matte/sil}} = \ln \left(\frac{X_{\text{Pt}}^{\text{matte}}}{X_{\text{Pt}}^{\text{sil}}} \right) \quad (13)$$

The effect of Fe on the solubility of Pt in matte can be eliminated by normalizing the solubility of PtS in the matte to unit activity of Pt, using the appropriate values for $a_{\text{Pt}}^{\text{matte}}$

from Table 3. An expression can then be derived to calculate the molar fraction of PtS in the matte (at unit activity) as a function of f_{S_2} $a_{\text{Pt}}^{\text{matte}} = 1$.

$$a_{\text{Pt}} = 1 \rightarrow \left(\frac{\Delta G(8)}{RT} - \ln \gamma_{\text{PtS}}^{\text{matte}} \right) = \ln X_{\text{PtS}}^{\text{matte}} - \ln f_{\text{S}_2} \quad (14)$$

The equation above shows that if we plot activity normalised $\ln X_{\text{PtS}}^{\text{matte}}$ as a function of $\ln f_{\text{S}_2}$, the y intercept in this plot is $\frac{\Delta G(8)}{RT} - \ln \gamma_{\text{PtS}}^{\text{matte}}$, which in this case equals -0.346 (Fig. 6). Moreover, the slope of the fit shown in Fig. 6 is $\sim 1/2$, which is the expected value when Pt dissolves in the matte as PtS. Therefore:

$$\ln X_{\text{PtS}}^{\text{matte}} = 0.47 \ln f_{\text{S}_2} - 0.346 \quad (15)$$

The solubility of Pt in a silicate melt at 1300 °C can be described by the following equation [Ertel et al. \(1999\)](#):

$$[\text{Pt}]_{\text{sil}}(\text{ppb}) = 2100f\text{O}_2 + 10980f\text{O}_2^{1/2} \quad (16)$$

From Eq. (16), the molar fraction of PtO in the silicate melt can be calculated as a function of $f\text{O}_2$. This procedure gives $\frac{-\Delta G(10)}{RT} - \ln \gamma_{\text{PtO}}^{\text{sil}} = -12.5$ and a slope of 0.5, yielding:

$$\begin{aligned} \ln X_{\text{PtO}}^{\text{matte}} &= \left(\frac{-\Delta G(10)}{RT} - \ln \gamma_{\text{PtO}}^{\text{sil}} \right) \\ &= \ln X_{\text{PtO}}^{\text{sil}} - \frac{1}{2} \ln f\text{O}_2 = 12.5 \iff \ln X_{\text{PtO}}^{\text{sil}} \\ &= \frac{1}{2} \ln f\text{O}_2 - 12.5 \end{aligned} \quad (17)$$

Eqs. (15) and (17) can be combined to derive an equation for $D_{\text{Pt}}^{\text{matte-sil}}$ as a function of both $f\text{S}_2$ and $f\text{O}_2$ at unit activity of Pt:

$$\ln D_{\text{Pt}}^{\text{matte/sil}} = Q \left[0.47 \ln f\text{S}_2 - \frac{1}{2} \ln f\text{O}_2 + 12.15 \right] \quad (18)$$

where Q is a constant to convert from $\frac{X_{\text{PtS}}^{\text{matte}}}{X_{\text{PtO}}^{\text{sil}}}$ into $\frac{X_{\text{Pt}}^{\text{matte}}}{X_{\text{Pt}}^{\text{sil}}}$.

5.6. Extrapolation to natural systems: possible effects of S and Fe

Eq. (18) is derived by combining our results on Pt solubility in Fe–S–O mattes with experiments on the solubility of Pt in simple-system silicate melts that lack both Fe and S, two elements that have a strong geochemical affinity for Pt. This raises the question of whether these two elements, when present at their normal abundance in natural silicate melts, can affect the solubility of Pt sufficiently to invalidate our approach. The matter was considered by [O'Neill et al. \(1995\)](#), who concluded that the effects of neither Fe nor S would be large. As there have been several developments since 1995 that add weight to this conclusion, it is worth recapitulating the arguments here.

The thermodynamics of S dissolving as sulphide (S^{2-}) in silicate melts are well understood (see discussion in [O'Neill](#)

and [Mavrogenes \(2002\)](#)). Under moderate to low oxygen fugacities, such as are appropriate for terrestrial basalts, S^{2-} dissolves by replacing O^{2-} on the anion sublattice, as shown experimentally by the variation of S solubility with $(f\text{O}_2/f\text{S}_2)^{1/2}$, which relationship has been found valid for every composition of silicate melt investigated, both Fe-containing and Fe-free ([O'Neill and Mavrogenes, 2002](#)). This relationship allows one to define a sulphide capacity C_S :

$$\ln C_S = \ln[\text{S}] + 1/2 \ln(f\text{O}_2/f\text{S}_2) \quad (19)$$

It has been shown experimentally that dependence of C_S on the composition of the melt is given by a relationship of the form:

$$\ln C_S = A_0 + \sum_M X_M A_M \quad (20)$$

where X_M are the mole fractions of cations M in the silicate melt, and the coefficients A_M are related to the difference in the chemical potentials of the components M_2O and M_2S in the silicate melt, which are in turn expected to be related, at least approximately, to the standard chemical potentials of the component oxide (or silicate) and sulphide, i.e.:

$$A_M = (\mu_{\text{M}_2\text{O}} - \mu_{\text{M}_2\text{S}})/RT + \text{constant} \quad (21)$$

(for a full derivation, see [O'Neill and Mavrogenes, 2002](#), their Eqs. 6 to 19). This relationship shows qualitatively that the reason why Fe has such a strong influence on sulphide solubility in silicate melts is simply because FeS is more stable, thermodynamically, than FeO ([O'Neill and Mavrogenes, 2002](#)). [Evans et al. \(2008\)](#) have recently presented the experimental evidence for a similar relationship for some other chalcophile elements, namely Mn, Ni and Cu.

This experimentally tested thermodynamic model describing the effect of a cation M^{2+} in a silicate melt on S^{2-} solubility may be inverted rigorously (i.e., via the Gibbs–Duhem relationship) to calculate the influence of S^{2-} in the silicate melt on the activity coefficient of M_2O . Although we cannot use this approach to calculate the effect of S^{2-} on PGE components because the solubilities of PGE cations in silicate melts are not great enough to have a discernible influence on S solubilities, this approach nevertheless permits the question to be posed in a way that is amenable to quantitative reasoning. As pointed out in [O'Neill et al. \(1995\)](#) – see his Eqs. 13 and 14), the change in the activity coefficient of the component Pt_xO in the silicate melt from substitution of S^{2-} for O^{2-} on the anion sublattice, relative to its activity in S-free melt of otherwise the same composition, is given by:

$$\gamma_{\text{Pt}_x\text{O}}^{\text{melt},+\text{S}} / \gamma_{\text{Pt}_x\text{O}}^{\text{melt,no S}} = \exp \left\{ \sum_M X_M X_S \Delta \mu_{\text{rec}}^{\text{Pt-M}} / RT \right\} \quad (22)$$

where $\Delta \mu_{\text{rec}}^{\text{Pt-M}} = (\mu_{\text{Pt}_x\text{O}} - \mu_{\text{Pt}_x\text{S}}) - (\mu_{\text{M}_2\text{O}} - \mu_{\text{M}_2\text{S}})$, $\sum_M X_M = 1$, and X_S is the fraction of S^{2-} on the anion sublattice. For a silicate melt with 1000 ppm S and 45 wt% O, $X_S = 0.001$. The question then boils down to what is a physically reasonable range in which values of $\Delta \mu_{\text{rec}}$ may fall? From the experimental S^{2-} solubility measurements summarized in Table 12 of [O'Neill and Mavrogenes, 2002](#)),

Fig. 6. Molar fraction of PtS in matte as a function of $f\text{S}_2$.

we find that values of cations with the largest interactions with S, namely Fe^{2+} and Mn^{2+} , have values of A_{Fe} and A_{Mn} that are ~ 20 relative to non-chalcophile cations like Ca^{2+} and Mg^{2+} (i.e., $A_{\text{Fe}} - A_{\text{Ca}}, \approx 20$, etc. – see Table 12 in O'Neill and Mavrogenes, 2002). If we adopt this extreme value for Pt then we obtain $\gamma_{\text{Pt},\text{O}}^{\text{melt},\text{S}}/\gamma_{\text{Pt},\text{O}}^{\text{melt},\text{no S}} \sim \exp\{20 \times 0.001\}$, or 2%, which is trivial given that even a factor of 10 change in $\gamma_{\text{Pt},\text{O}}^{\text{sil}}$ would not effect our arguments. Note that the thermochemical data for PtO_2 and PtS_2 (Barin, 1989) suggest values of $\Delta\mu_{\text{rec}}/RT$ that are actually much less 20, so even the 2% is likely to be overestimated.

In considering the possible effect of adding Fe to the simple-system silicate melts, we note first that there is nothing in the known chemical properties of PGE cations to expect any strong chemical interactions with Fe^{2+} (or Fe^{3+}). The chemical properties of ionic substances are of course quite different from those of the elements from which they form, so there is no rational reason to expect that the large interactions between Pt and Fe in the metallic state should carry over into interactions between Pt^{x+} and Fe^{2+} in silicate melts. Ternary oxide compounds involving Pt^{x+} and Fe^{2+} are not known, so there is no reason to suppose that they might be unusually stable. Unlike for S, there is now some experimental evidence for whether the presence of Fe in a silicate melt has a noticeable effect on the solubilities of some other PGEs, although Pt itself has not been studied explicitly. The issue was briefly reviewed by Borisov and Palme (2000), who quote direct evidence from the experimental study of Borisov et al. (1992), which demonstrated no difference in Ir solubilities between Fe-free melts and those containing up to 20 wt% “FeO” (total Fe as FeO), whereas the study of Capobianco and Hervig (1996) found only a modest effect of Fe on Pd solubilities. Since then, Brennan et al. (2005) have studied the solubilities of Ir, Os and Au in high-FeO melts using laser-ablation ICP–MS as the analytical method, which of course has the advantage that nanonuggets would be detected if present. This study shows convincingly from nugget-free experiments that the solubilities of these elements are comparable to, or lower than, those in Fe-free compositions. The lower solubility of Ir found by Brennan et al. (2005) in their melts compared to O'Neill et al. (1995) in Fe-free anorthite-diopside eutectic melt is likely due to the much higher concentration of CaO in the latter, since basic oxide components like CaO are expected to enhance the solubility of high-valence cations like Ir^{3+} (e.g., O'Neill and Eggins, 2002). The lack of any effect of FeO on the solubility of Re, another Highly Siderophile Element, has recently been documented by Mallmann and O'Neill (2007).

6. DISCUSSION

As discussed previously, the assumption that $D_{\text{Pt}}^{\text{matte-sil}}$ lies appreciable below the value required for the magmatic hypothesis for Pt-rich ore deposits has lead to a number of ad hoc models to explain the origin of Pt-rich horizons in layered mafic intrusions (e.g., the Merensky Reef). However, our results as well as those from Pruseth and Palme (2004) have shown that $D_{\text{Pt}}^{\text{matte-sil}}$ is larger than previous estimates by up to five orders of magnitude. The likely expla-

nation is that the previous estimates were compromised by unrecognized nanonugget contamination, as they were performed under conditions that are in no significant way different from our experiments in which the equilibrium solubility of PGEs is completely obscured by nanonuggets. The nanonugget contamination is clearly revealed by laser-ablation ICP–MS analysis.

Our high calculated $D_{\text{Pt}}^{\text{matte-sil}}$ values are in good agreement with calculated values for other PGE (Ru – Andrews and Brennan, 2002; Os – Brennan, 2008). Here we discuss some of the implications of very high $D_{\text{Pt}}^{\text{matte-sil}}$, and consequent high enrichment of a matte in Pt, to the enrichment models used to explain PGE-rich horizons associated with mafic intrusions.

6.1. The relationship between the matte/silicate-melt mass ratio (R), and $D_{\text{Pt}}^{\text{matte-sil}}$

The difference between the $D_{\text{Pt}}^{\text{matte-sil}}$ proposed in this study, and the much lower values proposed earlier by Helz and Rait (1988), Peach et al. (1990, 1994), Stone et al. (1990), Fleet et al. (1991, 1996), and Crocket et al. (1997), has implications for genetic models for Pt-rich horizons in large layered intrusions such as the Merensky Reef. If an element i partitions between a sulphide-rich matte and a silicate melt of finite volume, it can be shown that the concentration of i in the matte (Y_i) is given by (Campbell and Naldrett, 1979):

$$Y_i = X_i^0 D_i (R + 1) / (R + D_i) \quad (23)$$

where X_i^0 is the original concentration of i in the silicate melt, R is the silicate-melt/sulphide-matte mass ratio, and D_i the distribution coefficient of i between sulphide-rich matte and silicate melt. Re-arranging the equation in terms of R yields:

$$R = [D_i (Y_i/X_i^0 - 1)] / [D_i - Y_i/X_i^0] \quad (24)$$

where Y_i/X_i^0 is the apparent partition coefficient for the element i , called here the empirical partition coefficient (D_i^a). Substituting D_i^a into equation 24 yields:

$$R = [D_i (D_i^a - 1)] / [D_i - D_i^a] \quad (25)$$

From Eq. (24), R can be plotted as a function of D_i for different values of D_i^a (Fig. 7). Three observations can be made from Fig. 7:

- (1) When $D_i > 10R$, $R \sim D_i^a$, and independent of D_i ;
- (2) When $R \leq D_i \leq 10R$, D_i^a depends on both D_i and R ;
- (3) When $D_i < 10R$, D_i^a depends on D_i and is independent of R .

D_{Pt}^a for the Merensky Reef is between 10^4 and 10^5 (e.g., Campbell et al., 1983). When $D_{\text{Pt}}^{\text{matte-sil}}$ is significantly smaller than 10^5 (Helz and Rait, 1988; Peach et al., 1990, 1994; Stone et al., 1990; Fleet et al., 1991, 1996; Crocket et al., 1997), then D_{Pt}^a will depend on $D_{\text{Pt}}^{\text{matte-sil}}$. On the other hand, if $D_{\text{Pt}}^{\text{matte-sil}}$ is much larger than D_{Pt}^a , (this study, Pruseth and Palme, 2004; Bezmen et al., 1991), then D_{Pt}^a equals R and is independent of $D_{\text{Pt}}^{\text{matte-sil}}$.

6.2. Should elemental PGE ratios in magmatic sulphides reflect differences in their $D_{\text{PGE}}^{\text{matte-sil}}$?

It has been noted that the Pt/Pd of the Merensky Reef sulphides is equal to the ratio of the silicate melt it separated from (Davies and Tredoux, 1985). It has been argued that because $D_{\text{Pt}}^{\text{matte-sil}}$ is unlikely to be equal to $D_{\text{Pd}}^{\text{matte-sil}}$, the observation that $(\text{Pt/Pd})_{\text{matte}} \sim (\text{Pt/Pd})_{\text{sil}}$ is inconsistent with a magmatic hypothesis for the Merensky Reef sulphides (Ballhaus and Ryan, 1995). This argument is valid only if $D_{\text{Pt}}^{\text{matte-sil}}$ and $D_{\text{Pd}}^{\text{matte-sil}} < R$. However if $D_{\text{Pt}}^{\text{matte-sil}}$ and $D_{\text{Pd}}^{\text{matte-sil}} \gg R$, it can be shown (see Eq. (27) below) that the Pt/Pd in the matte is approximately equal to the Pt/Pd of the silicate melt it separated from.

Preliminary experiments where the solubility of Pd in mattes was investigated show that Pd is more compatible with the matte with respect to the metal phase than Pt. However, it was not possible to saturate a matte in Pd within the range of experimental conditions studied. For the purposes of this discussion a minimum $D_{\text{Pd}}^{\text{matte-sil}}$ of 1 will be assumed. At QFM, $D_{\text{Pd}}^{\text{matte-sil}} = 3 \times 10^8$ (Borisov et al., 1994). By dividing $D_{\text{Pd}}^{\text{matte-sil}}$ with $D_{\text{Pd}}^{\text{metal-matte}}$, we obtained a $D_{\text{Pd}}^{\text{matte-sil}} > 3 \times 10^8$.

Eq. (23) can be expressed as the ratio between the concentrations of Pt and Pd in the sulphide-rich matte ($Y_{\text{Pd}}/Y_{\text{Pt}}$):

$$\frac{Y_{\text{Pd}}}{Y_{\text{Pt}}} = \frac{X_{\text{Pd}}^0 D_{\text{Pd}}^{\text{matte-sil}} (R+1) / (R + D_{\text{Pd}}^{\text{matte-sil}})}{X_{\text{Pt}}^0 D_{\text{Pt}}^{\text{matte-sil}} (R+1) / (R + D_{\text{Pt}}^{\text{matte-sil}})} \quad (26)$$

Assuming that $(R+1) \sim R$ and because $D \gg R$, then $(R+D) \sim D$:

$$\frac{Y_{\text{Pd}}}{Y_{\text{Pt}}} = \frac{X_{\text{Pd}}^0 D_{\text{Pd}}^{\text{matte-sil}} R / D_{\text{Pd}}^{\text{matte-sil}}}{X_{\text{Pt}}^0 D_{\text{Pt}}^{\text{matte-sil}} R / D_{\text{Pt}}^{\text{matte-sil}}} \quad (27)$$

Eq. (27) shows that if both $D_{\text{Pt}}^{\text{matte-sil}}$, $D_{\text{Pd}}^{\text{matte-sil}} \gg R$, the Pt/Pd ratio of the sulphide-rich matte is the same as in the parental silicate magmas and is independent of the difference between $D_{\text{Pd}}^{\text{matte-sil}}$ and $D_{\text{Pt}}^{\text{matte-sil}}$. As a consequence, if $D_{\text{Pt}}^{\text{matte-sil}}$ and $D_{\text{Pd}}^{\text{matte-sil}}$ are both greater than 10^7 , as this study suggests, the similarity between the Pt/Pd ratio in the

Merensky Reef and the silicate melt it crystallised from cannot be used to argue against an magmatic origin for PGE-rich horizons in layered intrusions, but rather provides strong evidence in support of this hypothesis.

6.3. Matte/silicate-melt equilibrium as the primary cause for PGE enrichment in mafic layered intrusions

Our high-temperature, supra-liquidus experiments show that the partition coefficients for Pt and the other PGE into sulphide mattes are well above the level required for the magmatic hypothesis to explain the PGE enrichment in Pt-rich horizons in layered intrusions. However, the highly chalcophile nature of Pt and other PGE in magmatic systems does not preclude the possibility that sulphides and PGE may be remobilized under subsolidus or near solidus conditions by deuteric or metasomatic fluids. Remobilization of sulphides by late stage fluids would undoubtedly modify the primary sulphide textures found in PGE-rich horizons in layered intrusions. The action of late fluids would be felt more strongly by phases with lower melting points, especially those that are soluble in hydrothermal fluids. In this respect sulphides are particularly vulnerable, and have been shown to be easily remobilized during low temperature metasomatism (e.g., Luguet et al., 2008). The remobilization of sulphides would leave behind the less mobile PGE, more refractory PGE-rich phases (platinum group minerals – PGM), giving the appearance that the fluids themselves were responsible for the initial enrichment (Godel et al., 2006, 2007). Even though fluids may locally remobilize the PGE, Wood (1987) in his experimental study of PGE solubilities in brine-rich fluids, argued that Pt and Pd solubilities in fluids are too low to be consistent with the observed enrichments found in layered mafic intrusions. Moreover, base metals such as, Fe, Cu and Ni were shown to be over an order of magnitude more mobile than the PGE, which would cause an enrichment of base metals over the PGE. In PGE-rich horizons associated with mafic intrusions PGE tend to be greatly enriched relative to the base metals (see for example, Naldrett et al., 1987).

In light of the above discussion, it is possible to reconcile the textural evidence of metasomatism in mafic layered intrusions (e.g., Mathez, 1995), with the primary enrichment in Pt, at supra-liquidus conditions, of a sulphide-rich matte relative to a silicate melt.

ACKNOWLEDGMENTS

We would like to thank Michael Shelley and Charles Magee, for providing invaluable assistance during ELA-Q-ICP-MS work; Ashley Norris for his assistance while using of the CAMECA-SX100 electron microprobe; Guilherme Mallmann, Chris Ballhaus and Ambre Luguet for their insightful reviews and comments. We thank Ed Ripley's editorial handling, and Ed Mathez, Alan Boudreau and an anonymous reviewer for their thorough reviews.

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Fig. 7. Dependence of D_{Pt}^a on R and $D_{\text{Pt}}^{\text{matte-sil}}$. If $D_{\text{Pt}}^{\text{matte-sil}} < R$, D_{Pt}^a depends on $D_{\text{Pt}}^{\text{matte-sil}}$. If $D_{\text{Pt}}^{\text{matte-sil}} > R$, D_{Pt}^a depends on R and is independent of $D_{\text{Pt}}^{\text{matte-sil}}$.

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Associate editor: Edward M. Ripley