Solubilities of Pt and Rh in a haplobasaltic silicate melt at 1300°C

W. ERTEL,1,2 H. ST. C. O’NEILL,2-*, P. J SYLVESTER,2,† and D. B. DINGWELL1
1Bayerisches Geoinstitut, Universita¨t Bayreuth, D-95440 Bayreuth, Germany
2Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

Abstract—The solubilities of Platinum (Pt) and Rhodium (Rh) in a haplobasaltic melt (anorthite-diopside eutectic composition) have been determined experimentally by using the mechanically assisted equilibration technique at 1300°C, as a function of oxygen fugacity (10⁻¹² < fO₂ ≤ 1 bar), imposed by CO-CO₂, N₂-H₂-H₂O, Ar-O₂, and air gas mixtures. Samples were analyzed by sample nebulization (SN) inductively coupled plasma-mass spectrometry and, using some of these samples as standards, also by laser ablation (LA) inductively coupled plasma-mass spectrometry. The latter is a true microanalytical technique that allows small-scale sample heterogeneity to be detected. At each oxygen fugacity step, a time-series of samples was taken, to demonstrate that the solubilities converge on a constant value. In addition, solubilities were measured after both increasing and decreasing the imposed fO₂.

The results fall into three groups, according to oxygen fugacity. At high fO₂s, (fO₂ ≥ 10⁻² bars), samples are homogenous at all sampling scales. Both Pt and Rh predominantly dissolve in the silicate melt as Pt⁴⁺ and Rh³⁺ at the highest fO₂s studied (air and pure O₂). From these data, we obtained the following expressions for the solubilities of Pt and Rh:

\[
\text{Pt/ppb} = 2100(\text{fO}_2) + 10980(\text{fO}_2)^{1/2}
\]

\[
\text{Rh/ppb} = 68630(\text{fO}_2)^{3/4} + 31460(\text{fO}_2)^{1/2}
\]

At fO₂ < 10⁻⁵ bars, the true solubilities of Pt and Rh appear to be obscured by Pt-Rh micronuggets, which remain suspended in the melt despite stirring on time scales of 10⁷ h, resulting in samples that are heterogenous on the laser sampling scale. Samples at intermediate fO₂ (10⁻² to 10⁻⁵ bars) are affected by the micronugget problem on the sampling scale of the conventional SN-inductively coupled plasma mass spectrometry, but these can be filtered out by analyzing on the laser sampling scale.

1. INTRODUCTION

The platinum group elements (PGEs: Ru, Rh, Pd, Os, Ir and Pt), together with Re and Au, comprise a geochemical group known as the highly siderophile elements (HSEs), the defining characteristic of which is their high metal/silicate or sulfide/silicate distribution coefficients (D_M/sil or D_S/sil). The abundances of these elements in terrestrial rocks are generally extremely low, partly because the HSEs are heavy elements with intrinsically low cosmochemical abundances and partly because their high metal/silicate partition coefficients probably resulted in most of the Earth’s complement of these elements being partitioned into the core. Thus, the primitive mantle abundances of the HSEs range from 0.3 ppb (Re, which is the least abundant naturally occurring element in the silicate portion of the earth) to 8 ppb (Pt, the most abundant of the group). In fact, the concentrations of the HSEs in crustal rocks are usually even lower than their primitive mantle abundances because their high sulfide/silicate distribution coefficients mean that they tend to remain in residual sulfide during partial melting of the mantle.

Nevertheless, recent advances in analytical geochemistry have enabled the concentrations of the HSEs to be determined accurately in basaltic and ultramafic rocks. This has stimulated experimental investigation into their high-temperature geochemical properties, starting with attempts to quantify their partitioning behavior among metal, sulfide, and silicate melt phases. However, high values of D_M/sil and D_S/sil, which characterize the HSEs, are inherently difficult to measure accurately because contamination of the silicate phase with even a tiny amount of metal or sulfide may be sufficient to overwhelm the true amounts in the silicate phase.

Two experimental approaches currently are being used. The first type of approach comprises direct attempts at measuring metal/silicate or sulfide/silicate distribution coefficients between phases with compositions closely approximating naturally occurring compositions. This approach has resulted in apparent values of both D_M/sil and D_S/sil that cover a surprisingly narrow range of values between 10⁶ and 10⁸ for all the HSEs, at nearly all investigated conditions. This narrow range is not expected from basic thermodynamic considerations (e.g., O’Neill et al., 1995; O’Neill and Nell, 1997) because the standard state thermodynamic properties of HSE oxides are sufficiently different for larger order-of-magnitude differences in distribution coefficients to be expected. Moreover, such experiments have not demonstrated any clear relationship between D_M/sil or D_S/sil and variables such as oxygen fugacity or temperature. This gives rise to the suspicion that at present the “direct” experiments are effectively measuring the physical...
limits of metal/silicate or sulfide/silicate separation, rather than true thermodynamic equilibrium. Hitherto, there has been no effective microanalytical technique that could reveal small scale inhomogeneities in such samples. These difficulties promote the need for somewhat more indirect approaches, which seek to measure the fundamental thermochemochemical quantities upon which the partitioning equilibria are assumed to depend. In the most direct of these indirect methods, the solubility of an element \( M \) (either pure or in a simple alloy) is measured in a silicate melt of composition analogous to a natural basaltic melt but simplified in composition such that it does not contain Fe or other siderophile elements (e.g., Borisov et al., 1994; Borisov and Palme, 1997; O’Neill et al., 1995). These solubilities may be converted to metal/silicate distribution coefficients by using the relationship:

\[
D^\text{Fe-silicate}_M = \frac{1}{AM} \cdot \frac{a^{Fe,\infty}_M}{a^{M}_{Fe,\infty}} \tag{1}
\]

where \( a^{Fe,\infty}_M \) is the activity coefficient of \( M \) in Fe-rich metal at infinite dilution, a quantity that is usually available in the literature but is in any case measured comparatively easily. For all HSEs except Au, \( a^{Fe,\infty}_M < 1 \) (O’Neill et al., 1995), which contributes to the high values of \( D^\text{Fe-silicate}_M \). Values of \( D^\text{Fe-silicate}_M \) could in theory be calculated similarly, but extra information on the stability of \( M \) in the sulfide phase would be needed. This approach assumes Henry’s Law for the HSE in the silicate melt, which is a reasonable assumption considering the low solubilities involved and that the HSE-Fe alloy is Fe-rich. The analogous calculation for conditions in which a less Fe-rich alloy may be in equilibrium with the silicate melt are made readily.

This approach has the advantages that the concentrations of the element \( M \) in the silicate melt are obviously orders of magnitude higher than in the “direct” experiments, greatly facilitating the chemical analysis of the melts and that the solubility can be measured over an extremely wide range of oxygen fugacity, thereby giving information on the valence state or states of \( M \) in the silicate melt, which is the fundamental property controlling the geochemical properties of \( M \) as a trace element. What at first sight might seem a disadvantage of the solubility method, that an HSE might perhaps dissolve in natural, Fe-containing, silicate melts by a different mechanism to that in simple systems (e.g., by complexing of the HSE with Fe in the silicate melt), should be another incentive for carrying out such experiments: for, if such a different mechanism is important, it needs to be identified and understood. This can only be done by comparing results for Fe-containing and Fe-free systems.

In this study, we present new data on the solubilities of both Pt and Rh in a hapolbasitic (anorthite-diopside eutectic) melt at 1300°C, as a function of oxygen fugacity. A similar experimental study on Pt solubilities recently has been presented by Borisov and Palme (1997), but Rh solubilities have not been investigated hitherto in this way. However, the important experimental innovation presented here is the development of the experimental silicate glasses by using a true microanalytical technique, namely laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This has enabled us to assess the homogeneity of the glasses with respect to Pt and Rh on a submicron scale, providing a more reliable guide as to whether measured concentrations represent true solubilities.

## 2. Experimental

### 2.1. Sample Equilibration

The solubilities of Pt and Rh were determined by using the stirred-crucible technique, as described in Dingwell et al. (1994), O’Neill et al. (1995), and Ertel et al. (1996). Approximately 100 g of diopside-anorthite eutectic melt composition was loaded into a 20 wt.% Rh–80 wt.% Pt crucible, which was placed in the hot zone of a conventional gas mixing vertical tube furnace (see figure 1 in Dingwell et al., 1994). To facilitate equilibration, the melt in the crucible was stirred by a 20 wt.% Rh–80 wt.% Pt spindle, operated by a small electrical motor. Samples of melt taken immediately after loading the crucible were analyzed for bulk Pt and Rh (see below) and found to contain 1 ppm of Pt and 0.4 ppm of Rh (experiment 1) and 120 ppb of Pt and 130 ppb of Rh (experiment 2).

Oxygen fugacity was controlled by using air, \( O_2 –Ar \), and \( CO–CO_2 \) gas mixtures. We also attempted a solubility determination at the end of the experiment by using a \( H_2 –H_2 O–N_2 \) mixture. The oxygen fugacity was measured by using a STROXYA stabilized zirconia oxygen sensor (Ceramic Oxide Fabricators, Australia), from which the output emf was monitored continuously throughout the experiment on a chart recorder. The maximum difference between the oxygen fugacities as calculated from the applied gas mixing ratio (using standard thermochemochemical data from Chase et al., 1985) and that read by the sensor was \(<0.2\) log-bar units, except at extreme \( CO_2/CO \) ratios (see Table 1).

The experiment can be sampled at any time by stopping the stirring, removing the spindle, and dipping an alumina rod into the melt. An amount of melt (typically 0.5–1 g) congeals around the cold alumina rod, which is then extracted quickly from the furnace and quenched into water. An important advantage of the experimental method is that the concentrations of Pt and Rh in the melt can be sampled in a time series, following each change in oxygen fugacity. The change of Pt and Rh concentrations in a smooth way toward steady-state values is a necessary requirement for demonstrating equilibrium but is not sufficient. Whether steady-state values always define a true chemical equilibrium in solubility experiments is a major theme of this investigation.

### 2.2. Analytical Methods

#### 2.2.1. Electron microprobe analyses

The major element compositions of selected samples were checked by electron microprobe analysis at the Bayerisches Geoinstitut (Bayreuth, Germany) using a Cameca SX 50 electron microprobe equipped with four wavelength-dispersive spectrometers and a PAP absorption correction program (Pouchou and Pichoir, 1984). The operating conditions were 15 kV of accelerating voltage, 15-nA current on brass, 20-s counting time, and a defocused beam. Standards were wollastonite (Ca), enstatite (Mg), spinel (Al), and orthoclase (Si). The measurements showed no change in composition during the entire experiment. The average major element composition of the selected samples was 50.76% SiO₂, 23.10% CaO, 10.89% MgO, and 15.25% Al₂O₃ (analysis normalized to 100%), which is in excellent agreement with the ideal composition of the An-Di eutectic composition of 50.34% SiO₂, 23.48% CaO, 10.80% MgO, and 15.38% Al₂O₃.

#### 2.2.2. Analysis of Pt and Rh

The concentrations of Rh and Pt in the experimental glasses were determined either by one or by both of two methods of ICP-MS: 1) conventional pneumatic nebulization (SN-ICP-MS) of aliquots of dissolved sample, and 2) laser ablation of the sample itself (LA-ICP-MS). The advantage of the first method is that it has good accuracy and low limits of detection (<1 ppb) and the standardization procedure is against standard solutions and is straightforward (i.e., there is no need for “matrix” corrections that depend on the composition and/or physical state of the sample). However, the disadvantages are that it requires what is by experimental standards a relatively large amount of sample, and, most importantly, it cannot give much information on the homo-
The returned to the hot plate for another day. The solutions then were to an ultrasonic bath for 1 h to enhance disaggregation and were beaker on a hot-plate at 140°C. After 1 day, the beakers were removed ml of concentrated HF in a covered 25-ml Savillex screw-top Teflon quenched samples were weighed on a microbalance and dissolved in 3 nebulization (SN-ICP-MS). Glass pieces (30 – 80 mg) broken from the instrument (Loughborough, UK). In the first technique, samples were some of the glass samples analysed by SN-ICP-MS (specifically, those to that of the samples themselves. Here, ideal standards are provided by methods is that the analyses are matrix-dependent, requiring good sili- of PGE solubilities or partitioning behavior. Apart from higher detec- Because of this, it should be applicable to most of the previous studies 2.2.3. SN-ICP-MS analytical methods Both methods used a Fisons VG PlasmaQuad PQ2-XR ICP-MS instrument (Loughborough, UK). In the first technique, samples were introduced into the plasma as solutions by conventional pneumatic nebulization (SN-ICP-MS). Glass pieces (30 – 80 mg) broken from the quenched samples were weighed on a microbalance and dissolved in 3 ml of concentrated HF in a covered 25-ml Savillex screw-top Teflon beaker on a hot-plate at 140°C. After 1 day, the beakers were removed to an ultrasonic bath for 1 h to enhance disaggregation and were returned to the hot plate for another day. The solutions then were evaporated to incipient dryness, and the process was repeated with aqua regia (3 ml of concentrated HCl and 1 ml of concentrated HNO₃). The resulting residues were brought up to a total volume of 30 to 80 ml (for a dilution factor of 1000) in 1 N HCl. Two blanks were prepared in exactly the same way as the unknowns. For external calibration, two standard solutions, each containing known concentrations (~20 ng/g) of Rh or Pt, were made up in 1 N HCl just prior to analysis by diluting concentrated (100 μg/ml), ultra-high-purity, single-element 10% HCl solution standards obtained from Plasma Chem Corp (Farmington, NL). For internal standardization, a 1-N HCl solution of Be, In, and Tl was added to the sample, blank, and standard solutions so that each contained 10 ng/g each element. All concentrated acids used were double-distilled in-house, and all water used for acid dilutions was passed through a Milli-Q ultra-pure (>18 MegaOhms) filtration system. Operating conditions for the SN-ICP-MS analyses were similar to those reported by Sylvester and Eggins (1997). All solutions to be analyzed were poured into clean, 12-ml plastic tubes and introduced into the ICP-MS by using a Gilson autosampler at a rate of ~0.75 ml/min. To ensure that analyte signals had become stable prior to the start of analysis, data collection was delayed until 2 min after the start of solution uptake. Data were collected over four separate, 60-s acquisitions. Between analyses of different sample solutions, the ICP-MS was washed out by the introduction of a dilute surfactant (0.5% Triton X-100) for 5 min, 1 N HCl for 4 min, and 2% HNO₃ for 10 min. Analyses of aliquots of the blank solution made between measurements of unknowns indicated that this combination of washes returned instrument blank levels to the elements of interest to those present at the start of the experiment. Isotopes measured were ²⁰Be, ⁶⁶Zn, ⁸⁷Sr, ¹⁰⁰Rh, ¹¹⁶In, ¹⁹⁷Hf, ¹⁹⁹Pt, and ²⁰⁸Tl. Measurements for Zn, Sr, and Hf were used to make isobaric interference corrections for ⁶⁶Zn/⁶⁸Zn, ⁸⁷Sr/ ⁸⁶Sr, ⁸⁷Sr/⁸⁴Sr, and ¹⁹⁷Hf/¹⁹⁸Hf/²⁰⁶Pb, made on Rh-Pt-free, Zn-Sr-Hf-spiked solutions. Pre-scans of sample solutions had shown the presence of large signals for Zn, Sr, and Hf. Other potential interfering elements such as Cu, which may form ⁶⁵Ar²⁰⁷Cu, were found to be trivial and were ignored. To minimize counting statistic errors on Rh and Pt, dwell times used for them (20.48 ms) were longer than those used for
potentially interfering elements (5.12 ms). Blank subtractions for the measured Rh and Pt isotopes amounted to <5%. Corrections of up to 20% for variations in instrument sensitivity over the course of the experiment were made by linear interpolation between the intensities of the measured isotopes of Be, In, and Tl. After application of the corrections, concentration calculations for Rh and Pt were carried out by reference to a linear relationship between concentration and analyte intensity defined by the external calibration standard and the origin. A concentration was calculated for each of the four acquisitions made on each unknown; the standard deviations of each set are a measure of precision and are typically <3% for homogenous samples at the 1-ppm level.

2.2.4. LA-ICP-MS analytical methods

An additional advantage of this method is that sample preparation is minimal, permitting a large number of experimental charges to be analyzed in a short time. To prepare for analysis, glass pieces simply were mounted in epoxy, polished to expose a fresh, flat surface, and cleaned with methanol. The same mounts were used for electron microprobe analysis. Detailed procedures used for PGE analysis by LA-ICP-MS in the Australian National University laboratory are described by Sylvester and Eggins (1997). The laser is a Lambda Physik LPX 120i pulsed ArF excimer (acton, MA), emitting at 193 nm with a nominal pulse width of 17 ns, FWHM, and a pulse-to-pulse stability of ±5%. Sample mounts are placed in a translational stage encased within an air-tight cell where laser ablation is carried out in a mixed argon–helium atmosphere. The ablated material is transported to the ICP through plastic tubing and via a gas-expansion chamber that homogenizes the gas-sample mixture. To reduce detection limits to ~0.5 ng/g for Rh and Pt in this study, ablation was carried out with a 200-μm diameter beam spot and a repetition rate of 50 Hz, producing excavation rates of the laser pits of 5 to 10 μm/s or 0.1–0.2 μm/pulse.

Isotopes measured were 43Ca, 103Rh, and 195Pt. Because of the "dry" plasma conditions of LA-ICP-MS, isobaric interferences of 87Sr 16O on 103Rh and 179Hf 16O on 195Pt were trivial and ignored. Each standard and unknown analysis lasted for ~2 min; the first minute was used to measure background count rates with the laser off and the second minute to measure analyte intensities produced during laser ablation. Background subtractions were <5%. For external calibration, a Rh and Pt glass charge analyzed by SN-ICP-MS was used as the standard. Using the known concentration of Ca in each sample, the intensity of 43Ca (0.13% of total Ca) was monitored as an internal standard to correct for differences in ablation yield from analysis-to-analysis and temporal variations in instrument signal intensity. A secondary correction (<10%) for the mass dependency of signal drift was made by linear interpolation between analyses of the Rh-Pt glass standard made at the start of an analytical session and analyses repeated after each set of 5 to 10 analyses of unknowns. Raw counts were converted automatically to counts-per-second (cps) data for each of ~1-s long "time slices" by a Fisons time-resolved computer software package. Element concentrations in unknowns (C_unw) were calculated by using the relation:

\[ C_{\text{unw}} = \left( C_{\text{std}} \right) \cdot \left( I_{\text{unw}} / I_{\text{std}} \right) \cdot \left( (C_{\text{std}} / C_{\text{unw}}) / I_{\text{std}} / I_{\text{unw}} \right) \]

where C_unw = the concentration of the internal standard element, in this case Ca, in the unknown; I_unw/I_std = the ratio in the unknown of the measured cps of an isotope of the element to be determined in the unknown relative to that of an isotope of the internal standard element, in this case 43Ca; C_std/C_unw = the ratio in the standard of the concentration of the element to be determined in the unknown relative to that of the chosen internal standard element, and I_unw/I_std = the ratio in the standard of the measured cps of an isotope of the element to be determined in the unknown relative to that of the chosen isotope of the internal standard element. Values used for I_unw/I_std and I_std/I_unw in the concentration calculations were taken as the means of those produced during each 60-s episode of ablation, excluding the more obvious spikes or "blips" in the count rates encountered in many of the low level Rh–Pt samples. Analytical precision was estimated simply as (σ_individual/nh), where σ_individual = the 1 σ SD of an individual time slice measurement of I_unw/I_std or I_std/I_unw, in the population used to calculate the mean and nh is the total number of time slice measurements used to calculate the mean.

Examples of the time-resolved mass spectra of a homogenous (high fO2) glass sample and of an inhomogenous (low fO2) sample are given in Figure 1. The background ion signals are due to long-lasting Ca, Rh, and Pt contamination of the sample cell and tubing produced during previous analyses. In addition, the 43Ca background signal includes contributions of polyatomic molecules such as 28ArHD and 13C15N16OH derived from the Ar carrier gas and ambient atmosphere. After the laser is shut off, Ca, Rh, and Pt signals drop down to the observed baseline levels rather quickly (20–30 ss) but then decay little further as the system is flushed with fresh Ar gas prior to the next analysis. Baseline levels often slowly but steadily increase over the course of an analytical session as the system becomes progressively contaminated. Proper background corrections therefore require monitoring baseline count rates immediately before each ablation.

2.2.5. Precision and accuracy of the two methods

Many samples were analyzed by both SN-ICP-MS and LA-ICP-MS, allowing a comparison between the two methods, as well as an empirical assessment of the precision and accuracy of each. The comparison is shown in Figure 2. There is excellent agreement between the two analytical methods for Pt at concentrations >1000 ppb, and for Rh at concentrations >200 ppb. At lower concentrations, there is a tendency for the SN-ICP-MS method to give systematically higher values. This is simply because, during integration of the ablation spectra of these samples, we have omitted the more obvious "blips," representing particles or "micronuggets" of Pt-Rh distributed stochas-
tically throughout the sample (see, e.g., Fig. 1b). This approach must obviously have the effect of yielding lower concentrations than those obtained by solution analysis, which presumably includes all Pt-Rh micronuggets within the sample. The largest differences are for Pt, for samples taken during the reduction from step 1 (in air) to step 2 (pure CO2).

In the first step of the first experiment (step 1, in air; see Fig. 4a below), equilibrium was fairly rapidly established, although we continued to take samples over an extended period to demonstrate that a steady-state had been achieved. We thus have a series of 11 replicate samples (numbers 1–5 to 1–16), which we analyzed by both methods. For Pt, the mean value by SN-ICP-MS was 4031 ppb with a SD of 99 ppb (2.5%), versus 3935 ppb by LA-ICP-MS, with a SD of 256 ppb (6.5%). For Rh, the results were 11952 ± 256 ppb (2.1%) vs. 11769 ± 588 ppb (5.0%). These SN-ICP-MS analyses were acquired in two sessions separated by several months, whereas the LA-ICP-MS analyses were acquired in three sessions, spread over 3 yr.

3. RESULTS

3.1. Steady-state Solubilities

A summary of the results, in the form of apparent steady-state solubilities of both Pt and Rh at each oxygen fugacity step, is given in Table 1, and plotted in Figure 3. These steady-state solubilities were obtained in either of two ways: where the data at one step are both sufficiently numerous and sufficiently reproducible (i.e., where the time series defines a smooth curve trending toward a constant value, as in Fig. 4a and b), the data were fitted by nonlinear least squares regression to a first-order rate equation of the form:

\[ C_M(t) = C_M(eq) + (C_M(0) - C_M(eq))e^{-kt} \]

where \( C_M(0) \) is the initial concentration of M in the melt established at the end of the previous fO2 segment, \( C_M(eq) \) is the steady-state (inferred equilibrium concentration), and k is the rate constant. The uncertainty in \( C_M(eq) \) given in Table 1 was obtained from the regression analysis. Where such a fit could not be made, the “steady-state” value was obtained by taking the mean of the final few readings obtained for that segment, and the quoted uncertainty is the SD of this mean. A full listing of the results for each individual step (145 samples) is available from the authors on request.

3.2. Solubility as a Function of fO2

The results fall into three groups, according to the oxygen fugacity of the step. We shall refer to these groups as the high, low, and intermediate oxygen fugacity groups, respectively. At high fO2s (fO2 \( \geq 10^{-2} \), imposed by Ar-O2 mixtures, air, and pure O2), the solubilities increased or decreased smoothly (as monitored by the time series) to their new well defined steady-state values on changing oxygen fugacity. Examples of such time series are shown in Figure 4a and b. The laser analyses of these samples showed them to be homogenous at the laser sampling scale (e.g., Fig. 1a), and the apparent variation between samples taken once the steady-state values had been reached is comparable to the variation observed by replicate analysis of any one sample; furthermore, this variation is also comparable to the theoretically estimated precision of the laser method (±5% at these concentrations). The steady-state values from these steps show a regular decrease of concentration with decreasing oxygen fugacity (Fig. 3) that are fit well by the simple theoretical relationship expected for metals dissolving in silicate melts as oxide components (see below).

At lower oxygen fugacities, (fO2 \( \leq 10^{-5.0} \), imposed by CO-CO2 or N2-H2-H2O gas mixtures), the results show quite different behavior. Laser-ablation microanalyses of these samples show irregular mass/time spectra, an example of which is illustrated in Figure 1b. Sometimes the mass/time spectra also contain obvious “blips,” corresponding to somewhat larger heterogeneities. Clearly these samples are heterogenous on the laser sampling scale, although often the good agreement between successive samples in a series indicates that they are homogenous on the sampling scale of the SN-ICP-MS analytical method. The expected decrease of solubilities with decreasing fO2 is no longer observed (Fig. 3); hence, the smooth pattern of increase or decrease of solubilities on changing fO2, exhibited by the higher fO2 data, cannot be demonstrated (e.g., see Fig. 4c), and we lose this valuable method of assessing whether a steady-state has been achieved.
3.3. Calculation of Solubility Constants by Using the High $fO_2$ Results

The results at higher $fO_2$ (steps 1 and 12a to 16) were fitted by nonlinear regression analyses to equations of the type:

$$[M_{\text{total}}] = (\Sigma Q^{M^x}(fO_2)^{x/4})/X^M_{\text{alloy}}$$

where $[M_{\text{total}}]$ is the analyzed concentration of Pt or Rh in the silicate melt, the $x$s are the possible valence states of $M$, and $Q^{M^x}$ are the solubility constants for each valence state $x$ to be determined in the regression. (The values of $Q^{M^x}$ can be identified physically as the solubilities of $M^{x+}$ cations at the $fO_2$ of the standard state, pure O$_2$). For real experimental data with nonnegligible uncertainties, the choice of which values of $x$ to include in the regression are not always unambiguously determined by the data alone, and the choice of $x$ values needs to be guided by independent chemical knowledge. Here, we assumed that $x$ was likely to be 4 and 2 for Pt, but mainly 3 with the possibilities of both 4 and 2 for Rh. The factor $X^M_{\text{alloy}}$, the mole fraction of $M$ in the alloy, normalizes the data to pure Rh and Pt, assuming ideal mixing in Rh-Pt alloys (a reasonable assumption from the Rh-Pt phase diagram). For the 20 wt.% Rh–80 wt.% Pt alloy used here, $X^\text{Rh}_{\text{alloy}} = 0.32$ and $X^\text{Pt}_{\text{alloy}} = 0.68$.

For Rh, we obtain $Q^{\text{Rh}^3+} = 68630 \pm 7530$ and $Q^{\text{Rh}^2+} = 31460 \pm 3820$ in ppb. The data were weighted assuming an uncertainty in log $fO_2$ of $\pm 0.01$, 1 SD, for the steps in air and pure O$_2$, and $\pm 0.02$ for the steps in Ar-O$_2$ mixtures, and a SD of 5% in $[\text{Rh}_{\text{total}}]$. With this weighting, the reduced chi-squared ($\chi^2_r$) for the seven fitted data is 1.19, indicating an excellent fit to the data. The data cannot be fitted adequately assuming only a single valence state of Rh: assuming only Rh$^{3+}$ gives $\chi^2_r = 12.1$, and assuming only Rh$^{2+}$ gives $\chi^2_r = 15.6$. Including Rh$^{3+}$ in the regression does not improve the fit, but the presence of a substantial fraction of Rh$^{4+}$ at the higher oxygen fugacities cannot be excluded either. Moreover, a fit to the data can be achieved with Rh$^{4+}$ and Rh$^{2+}$ alone, which is equally as good,
Solubilities of Pt and Rh

Fig. 4. Examples of time series. (a) Steps 1 and 2. Step 1 produced a series of homogenous glasses; those in step 2 contained micronuggets of Pt/Rh, which in this particular step could be filtered out from the LA-ICP-MS analyses. The SN-ICP-MS analyses nevertheless show good reproducibility from one sample to the next, indicating that the micronuggets are evenly distributed on this sampling scale. (b) Steps 12 to 16, homogenous glasses, analyzed by LA-ICP-MS only. (c) Steps 3 to 6, inhomogenous glasses; hence, the difference between the LA-ICP-MS and SN-ICP-MS analyses. Note how an impression of having reached a steady-state in most steps is nevertheless given by the SN-ICP-MS analyses.
statistically, as that with Rh$^{3+}$ and Rh$^{2+}$. This Rh$^{4+}$–Rh$^{2+}$ possibility does not seem likely, however, because although Rh$^{3+}$ is a well known oxidation state of Rh, Rh$^{2+}$ is the dominant one in oxides at high temperature in air (e.g., Nell and O’Neill, 1997). What is clear from the present data is that Rh$^{2+}$ is the dominant species in silicate melts except at the very highest fO$_2$ levels.

The high fO$_2$ data for Pt are slightly better fit with a small contribution from Pt$^{4+}$ (the common oxidation state of Pt in oxides in equilibrium with Pt metal) although most of the Pt is clearly in the divalent state. We obtain $Q_{\text{Pt}^{4+}} = 2100 \pm 860$ and $Q_{\text{Pt}^{2+}} = 10980 \pm 370$ ppb, with $x_n^2 = 3.7$, by using the same weighting of the data as for Rh. This high value of $x_n^2$ may indicate a larger uncertainty in the Pt analyses: an uncertainty of $\pm 10\%$, 1 SD would give a value of $x_n^2$ near unity.

The lower fO$_2$ data for both Rh and Pt are not compatible with the above evaluation. Despite apparently constant levels being reached at each fO$_2$ step in bulk samples (i.e., as analyzed by SN-ICP-MS) on our sampling time scale (typically 850 h, or approximately 6 wk, see Table 1, and the example in Fig. 4c), these “steady-state” values do not follow any pattern when plotted against fO$_2$ (Fig. 3). Moreover, as noted above, the LA-ICP-MS analyses reveal considerable heterogeneity in all these samples. Although puzzling, this behavior seems typical of PGEs in haplobasaltic melts, and the pattern of Figure 3 is similar to that found previously for Ir (cf. O’Neill et al., 1995, their Fig. 3). A possible exception to this strange behavior among the PGEs is Pd (see Borisov et al., 1994).

Step 2 (pure CO$_2$) is intermediate in oxygen fugacity between the well behaved high fO$_2$ regime and the micronugget-dominated low fO$_2$ regime and shows intermediate behavior, worthy of special comment. The SN-ICP-MS results show a fairly steady, steady decrease to well defined new plateau values for both Pt and Rh (Fig. 4c). These values are not, however, consistent with the trends established by the high fO$_2$ data (Fig. 3), and the subsequent LA-ICP-MS analyses of these samples clearly showed that they are inhomogenous on the scale of a laser pulse. In these particular samples, spikes of Pt and Rh from the micronuggets stood out clearly in the laser ablation spectra and thus could be filtered out with some assuredness. The filtered values also decrease to a well defined plateau (Fig. 4a). These latter plateau values agree well with the extrapolation of the high fO$_2$ data; the solubilities at log fO$_2$ = −2.9 calculated from the regressions of the high fO$_2$ data are 504 ppb for Rh, vs. 496(±35) ppb observed, and 267 ppb for Pt, vs. 237(±10) observed.

Step 9 (log fO$_2$ = −4.8), which is the next step down in oxygen fugacity from step 2 (pure CO$_2$), also fits quite well onto the trend established at high fO$_2$ (Rh: 44 ppb calculated vs. 49(±2) ppb observed by LA-ICP-MS; Pt: 29 ppb calculated, 59(±9) ppb observed). Also, the differences between the SN-ICP-MS and LA-ICP-MS values for these samples are not great. The implication is that equilibrium also had been approached in this step; perhaps this is due to the >3000 h of stirring under CO/CO$_2$ mixtures being sufficient to eliminate the worst of the micronuggets (cf. step 17, Fig. 5).

4. DISCUSSION

4.1. Disequilibrium in PGE Solubility Experiments and the “Nugget Effect”

The results of segments 4 to 9 as analyzed by SN-ICP-MS seem to indicate an increase in apparent steady-state concentrations with decreasing fO$_2$ (see Fig. 3). Because fO$_2$ in these segments is imposed by CO-CO$_2$ gas mixtures, this decreasing fO$_2$ is accompanied by increasing pCO, and we initially proposed that the apparent increase in solubility of Pt and Rh was caused by dissolution as carbonyl species, M(CO)$_x$ (Ertel et al., 1995). However, further segments (10 and 11) do not fit this theory, and we now think that the decrease in solubilities from step 4 to step 9 is simply a result of a continuing decrease over time and that steps 4 to 8 (and perhaps also step 9) had not in fact reached a true steady-state. The appearance of a steady-state was a false impression, caused in part by the greater relative scatter in the data at these conditions (e.g., Fig. 4c). It
is important to note that the time involved in going from the beginning of step 4 to the end of step 8 is 3021 h, or 126 days—quite a different timescale from that necessary to reach a steady-state at higher $fO_2$ (e.g., Fig. 4a and b).

To test further the carbonyl hypothesis, we changed the gas mixture to forming gas (5% $H_2$ in $N_2$) bubbled through an ice/water mixture (step 17). This gas imposes a low $fO_2$ with negligible $pCO$. The results, which are inconclusive in so far as a steady-state was not reached, are shown in Figure 5. Clearly, though, the timescale of the decrease in Pt and Rh solubilities is $>1000$ h, similar to that inferred for steps 4 to 8.

The ratio Pt/Rh in the low $fO_2$ segments is usually $\sim 3$, which is quite close to that in the bulk Pt$_{50}$Rh$_{30}$ alloy (i.e., Pt/Rh = 4). By contrast, the Pt/Rh ratio in the high $fO_2$ samples is $<1$. This is perhaps a clue, suggesting that the excess Pt and Rh in the low $fO_2$ experiments are present as small metal particles, which we propose to call “micronuggets.” An estimate of the size of these nuggets can be obtained as follows. The volume sampled by each step of 1 s in the ablation mass spectra of Figure 1 is $3 \times 10^{-8}$ cm$^3$ (the laser beam diameter is 200 $\mu$m, the depth ablated at each pulse is 0.1 $\mu$m, and the pulse rate is 10 Hz with the data being smoothed over 10 pulses). Hence, the mass sampled per second is $\sim 10^{-7}$ g. If we assume that the laser ablates one micronugget in 1 s (this assumption gives the maximum size of a micronugget) and that the micronugget raises the concentration of the PGE by 100 ppb, then the mass of this micronugget is $10^{-14}$ g. Assuming a density of 20 g/cm$^3$, its volume is then $5 \times 10^{-16}$ cm$^3$. Hence, its radius is 0.05 $\mu$m. This estimation of the size of the micronuggets in these experiments is in good agreement with the 0.05 to 0.2 $\mu$m deduced by Lindstrom and Jones (1996) for Ir micronuggets in samples from previous stirred crucible experiments, small aliquots ($10^{-5}$ to $10^{-4}$ g) of which were analyzed by high sensitivity micro-instrumental neutron activation analysis.

A radius of 0.05 $\mu$m corresponds approximately to the particle size of colloids. The analogy with colloids suggests that the micronuggets could be kept in suspension by surface tension effects or perhaps simply by Brownian motion. Although even smaller micronuggets may exist, they would not be responsible for the heterogeneity seen at the sampling volume of a laser pulse. Larger micronuggets produce much stronger “blips,” as in the samples produced under pure CO$_2$ (step 2), which can be filtered out of the LA-ICP-MS spectra fairly satisfactorily.

Particles with a radius of 0.05 $\mu$m are substantially larger than just a cluster of atoms but are nevertheless of a sufficiently small size that their surface properties (e.g., the interfacial energy between the particle and the surrounding melt) may influence greatly their thermochemical properties; hence, in binary or multicomponent metal systems, their composition. This might explain why the weight ratio of Pt/Rh in the low $fO_2$ samples is rather variable and not exactly 4 as in the bulk alloy. For example, in the samples from step 2 (pure CO$_2$), the well defined difference between the LA-ICP-MS and SN-ICP-MS analyses gives an estimate of the Pt/Rh ratio of the micronuggets of 2.5, with an uncertainty of $\pm 0.5$, (1 SD); this is significantly lower than in the bulk alloy. Lindstrom and Jones (1996) also observed that the micronuggets inferred to be present in their Ir solubility experiments must have had a composition considerably different from the bulk metal.

The size of the proposed micronuggets is below that discernible optically, and the chances of finding a 0.05-$\mu$m micronugget (maximum section area $7.5 \times 10^{-3}$ $\mu$m$^2$) at an average concentration of one per $3 \times 10^4$ $\mu$m$^2$ of glass surface (the area of the laser beam), by, e.g., SEM or TEM, would seem to be negligible (similar to the chance of finding a 2.5 by 0.01-cm needle on a 10 m$^2$ surface of haystack). Thus, the micronuggets are likely to remain hypothetically inferred entities, which are not directly observable.

One reviewer suggested that it is the constant stirring of the melt in our experimental method that keeps the micronuggets in suspension. However, the results of Borisov and Palme (1997) on the solubility of Pt using the conventional wire-loop method suggest the presence of a far worse micronugget problem (in the low $fO_2$ regime; see below) in an unstirred experimental environment. Two of us (H. St. C. O’Neill and P. J. Sylvester, unpublished results) have also attempted similar experiments by using Pt, Rh, and various Pt-Rh alloys as wire-loops; LA-ICP-MS analyses of a set of these samples held at the “intermediate” $fO_2$ of $10^{-3.1}$ bars for 213.5 h showed irremediable contamination by micronuggets (far worse than observed in this study), whereas a similar set of loops run in air seemed relatively free of the problem. Also, we clearly observed a decrease in the micronugget concentration in our stirred experiments over very long periods of time (e.g., step 17, Fig. 5). We conclude that stirring does not cause the problem but, rather, may be effective in decreasing the micronugget concentration.

Finally, we emphasize that the micronuggets contribute only 0.75 ppm of Pt and 0.3 ppm of Rh to the samples of step 2 (pure CO$_2$ atmosphere), the worst affected by the problem, and $<100$ ppm of Pt or Rh in most other samples. Thus, we expect that the problem would only be discernible in experiments in which metal solubilities are $<10$ ppm, at least in the stirred crucible type of experiment used in this study. Thus, the problem should not affect previous results on moderately siderophile elements such as W or Ni (Ertel et al., 1997; Dingwell et al., 1994). A background level of micronugget contamination might be present in samples from the high $fO_2$ group, too, but would not be detectable in these samples if the micronuggets contributed $<100$ ppb to either Pt or Rh, as in the low $fO_2$ regime. Contamination of the high $fO_2$ samples at the 100-ppb level would not significantly perturb our results.

4.2. Estimation of Metal/Silicate Distribution Coefficients

A typical basaltic, picritic, or komatiitic melt from the Earth’s mantle has $n_{Fe,Cr} = 0.1$ and would therefore be in equilibrium with Fe-rich metal at an oxygen fugacity 2 log-bar units below the Fe-“FeO” (iron-wüstite) oxygen buffer, i.e., at log $fO_2 = -12.7$ at 1300°C. Extrapolation of our high $fO_2$ results predicts solubilities at this $fO_2$ of Pt and Rh of 5 ppt and 14 ppt, respectively. These inferred solubilities can be converted to metal/silicate distribution coefficients by using Eq. 1 and values from the literature for $F_{Fe,Fe}^{Fe}_{mel/sil}$ of $3 \times 10^{-5}$ (Gudmundsson and Holloway, 1993), and for $F_{Rh,Fe}^{Fe}_{mel/sil}$ of $1.5 \times 10^{-2}$ (Swartzenbruber, 1984). We obtained $D_{Pt,Fe}^{Fe}_{mel/sil} = 7 \times 10^{-3}$ and $F_{Rh,Fe}^{Fe}_{mel/sil} = 5 \times 10^{12}$.

These values are of course based on a very large extrapolation, which assumes that lower oxidation states of Pt and Rh (i.e., Pt$^{1+}$, Rh$^{1+}$, or the neutral atoms Pt$^0$ and Rh$^0$) are insig-
nificantly soluble in silicate melts at the ppt level. However, minimum limits on the possible values of $D_{Pt}^{metal/sil}$ and $D_{Rh}^{metal/sil}$ can be estimated from the observation that the solubilities of Pt and Rh must be less than the observed levels, micronuggets and all, at low $f_O^2$. These levels are ~100 ppb, when corrected from the alloy to the pure metals. Hence, $D_{Pt}^{metal/sil}$ must be $>10^{11}$ and $D_{Rh}^{metal/sil}$ must be $>10^9$. For most petrological applications in the terrestrial environment, it is sulfide/silicate melt distribution coefficients that are required. These can be estimated from the present results, by using the relation:

$$D_{M}^{sulf/sil} = D_{M}^{metal/sil}/D_{M}^{metal/sulf}$$

Fleet and Stone (1991) determined $D_{M}^{metal/sulf}$ ~ $10^3$ and $D_{Rh}^{metal/sulf}$ ~ $10^2$, giving $D_{Pt}^{metal/sulf}$ ~ $>10^7$ and $D_{Rh}^{metal/sulf}$ ~ $>10^7$. This, however, strictly only applies for sulfide melts saturated in Fe-rich metal (i.e., with Fe/S > 1 in the Fe-S binary system).

### 4.3. Comparison With Previous Work

In the high oxygen fugacity regime, our results for the solubility of Pt are in good agreement with those of Borisov and Palme (1997) in An-Di eutectic melt, as shown in Figure 6. This congruence is all the more impressive as Borisov and Palme used a different experimental technique (the wire-loop method, with pure Pt rather than the Pt 80 wt.%/Rh 20 wt.% alloy used here) and analyzed their run products by a different method—instrumental neutron activation analysis.

Furthermore, like us, Borisov and Palme (1997) were unable to obtain reproducible solubility measurements at lower oxygen fugacity (e.g., as shown in their Fig. 1). In fact, below an $f_O^2$ of $10^{-5}$, they obtain apparent solubilities as high as 2000 ppb (in equilibrium with a Pt-Rh alloy), more than an order of magnitude above our levels under similar conditions. They also report these low $f_O^2$ samples to be heterogenous, like ours. However, because the size of sample needed for their instrumental neutron activation analysis analyses is several milligrams, their heterogeneities must be on a significantly larger scale than those implied by our laser-ablation analyses. This is perhaps not unexpected, as the larger-sized micronuggets might be presumed to be stirred out by our experimental technique. At intermediate $f_O^2$ levels ($10^{-6}$ to $10^{-7}$), the solubilities reported by Borisov and Palme (1997) are slightly greater than our inferred values, consistent with slight contamination by micronuggets, as in our experiments. Borisov and Palme (1997) discuss the earlier experimental work on Pt solubilities.

The only previous experimental results on Rh solubility in silicate melts of which we are aware is a single datum from Capobianco and Drake (1990) in a CMAS composition at 1450°C in air and four experiments by Capobianco et al. (1994) on Fe-bearing silicate melts at 1248 to 1276°C, at what we call “intermediate” $f_O^2$. Capobianco and Drake (1990) observed a concentration of 55 (±9) ppm Rh, similar in magnitude to our own results, from which we calculate a solubility in air, in equilibrium with pure Rh, of 37 ppm, albeit at 1300°C and in a very different composition CMAS melt. The Rh solubilities of Capobianco et al. (1994) appear variable and, at ~1 to 10 ppm, are much higher than is consistent with our data at similar $f_O^2$.

### 5. CONCLUSIONS

The results of this study show that both Pt and Rh are extremely siderophile, with metal/silicate distribution coefficients that are at least $>10^9$, and, for Pt, could be as high as $10^{16}$. These are inferred values; we would expect attempts at direct measurement of $D_{M}^{metal/sil}$ for Pt and Rh to be confounded by the micronugget problem.

This raises the question of whether “direct” experimental determinations of sulfide/silicate melt distribution coefficients also are affected by the same problem. There are several indications that even the most careful experimental work may be so affected. For example, the recent studies of Fleet et al. (1996) and Crocket et al. (1997) demonstrate extreme variability in “direct” experimental determinations of $D_{M}^{metal/sil}$ for Os, Ir, Ru, Pt, Pd, and Au, results typically covering three orders of
magnitude in $D_{nm}^{\text{liquid}}$. Moreover, there appears to be little difference in mean values of $D_{nm}^{\text{liquid}}$ of all six of these HSEs, contrary to what might be expected from the large differences in the standard state properties of these elements (e.g., O’Neill et al., 1995; O’Neill and Nell, 1997). Lastly, the amounts of HSEs reported in the silicate melts of such experiments are often in excess of those expected for the solubilities of the pure element, despite the fact that the activities of the element are very much less than that needed for saturation in the sulfide phase, i.e., $a_{M}^{\text{Sulf}} \ll 1$, referred to a standard state of pure M. (That the levels of Pt and Pd in the sulfides used Fleet et al. (1996) and Crocket et al. (1997) in their experiments are indeed orders of magnitude below saturation in Pt or Pd is indicated by the phase diagrams for the systems Pt-Fe-S and Pd-Fe-S—see Raghavan, 1988; also, because these experiments contained all six of the HSEs studied, plus Fe $\pm$ Ni, the metal phase in equilibrium with the sulfide at saturation would be a complex Fe-(Ni)-bearing alloy, rather than single phase M. Hence, although exact values of $a_{M}^{\text{Sulf}}$ in these experiments are not known, the supposition that $a_{M}^{\text{Sulf}} \ll 1$ relative to pure M seems secure). Are these experiments really reporting true chemical distribution coefficients, or do they reflect the level of contamination of the phase diagrams for the systems Pt-Fe-S and Pd-Fe-S—see Raghavan, 1988; also, because these experiments contained all six of the HSEs studied, plus Fe $\pm$ Ni, the metal phase in equilibrium with the sulfide at saturation would be a complex Fe-(Ni)-bearing alloy, rather than single phase M. Hence, although exact values of $a_{M}^{\text{Sulf}}$ in these experiments are not known, the supposition that $a_{M}^{\text{Sulf}} \ll 1$ relative to pure M seems secure). Are these experiments really reporting true chemical distribution coefficients, or do they reflect the level of contamination of the silicate by micronuggets on a short experimental time scale? Our inferred value of $D_{\text{m}}^{\text{liquid}}$ of $>10^8$ is obviously substantially greater than the values of $\sim 10^3$ claimed by Fleet et al. (1996) and Crocket et al. (1997). LA-ICP-MS analysis of the silicate in the run products of such “direct” experiments should be able to resolve this matter.

Finally, we draw attention to the extremely long timescales over which the micronuggets persist in our experiments; much longer than that required to reach chemical equilibrium (e.g., in the high FeO$_2$ samples). Might HSE micronuggets similarly persist in natural magmas and be an important control on HSE geochemistry? Recently, Ballhaus et al. (1998) have provided evidence that this may in fact be the case, by identifying micronuggets rich in Os-Ir-Pt, which they propose to be of magmatic origin, preserved in sulfides of the Merensky reef.

Acknowledgments—We thank Herbert Palme and two anonymous reviewers for helpful comments.

REFERENCES


