=== **GEOCHEMISTRY** ===

Palladium Solubility in Water-Bearing Silicate Melts: Evidence from Experimental Data

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One of the most interesting geological problems, bearing both theoretical and practical significance, is the study of PGE geochemistry in the formation of the Earth's crust and mantle and in differentiated mafic–ultramafic magmatic complexes, as well as in related PGM mineralization. An important part of this problem is the experimental study of PGE solubility in natural and model silicate melts depending on oxygen fugacity—the main parameter of redox conditions of the magmatic process. Increasingly greater attention has recently been focused on the role of fluids in these processes. However, most experimental studies of the solubility of PGE, including Pd, have been conducted in the absence of fluid [1–3]. It is of interest in this context to study the dependence of Pd solubility in water-bearing silicate melts on oxygen fugacity corresponding to natural mineral formation.

Pd solubility was studied in silicate (haplobasaltic) melt of a $Di_{55}An_{35}Ab_{10}$ composition (DAA) that is close to Di–An eutectics, a model analogue of basaltic magmas. Experiments were conducted in the Pd ampules at 1200°C, fluid pressure of 2 kbar, and f_{O_2} from HM to WI buffer. Hydrogen mole fraction varied from 0.05 to 0.50; $\log f_{O_2}$, from –2.6 to –11.8. To estimate the temperature dependence of Pd solubility, experiments were also performed at 1300°C, 2 kbar, and HM buffer.

Experiments were carried out in a high gas pressure apparatus using hydrogen reactor at the Institute of Experimental Mineralogy. The oxygen fugacity was controlled by the double capsule buffer technique in oxidizing conditions (HM–NNO buffers) and by an Ar–H2-gas mixture introduced into the hydrogen reactor of the high gas pressure apparatus in reducing conditions

(x_{H_2} >0.05) [4]. Temperature was measured by Pt30Rh/Pt6Rh thermocouples with an accuracy of ±7°C. Pressure was controlled using a Burdon manometer with an accuracy of ±50 bar. Experiments were quenched by switching off power at a rate of 130°C/min within 1200–800°C.

Experiments lasted for 24 h at HM buffer. Our kinetic experiments on Pd solubility and literature data [1–3] indicate that equilibrium is attained in 24 h at 1200°C even in the absence of aqueous fluid. Since water fugacity decreases under reducing conditions (at x_{H_2} > 0.05), the run duration was increased up to 72 h.

Samples were analyzed by the INAA method at Toronto University, Canada, with an accuracy of ±5 rel % using the technique described in [5].

The composition of the fluid was calculated using a special program, assuming that fluids under the experimental temperature and pressure (1200 and 1300°C, 2 kbar) behave as ideal mixtures of real gases. Data of Robie [6] and Mel'nik [7] were used for calculations.

Experimental glass was represented by transparent cylinders 6 mm across and 5–6 mm high. The top layer (0.1–0.5 mm) was removed by polishing in order to avoid Pd pollution of the glass surface.

The table lists experimental conditions and results: fugacity of fluid components and Pd solubility in the silicate melt. Figures 1–3 show the dependence of Pd solubility on oxygen and water fugacity and temperature.

It is seen from these data that Pd solubility at 1200°C widely varies depending on redox conditions, which are characterized by hydrogen mole fraction, as well as oxygen and water fugacity in the fluid. This indicates the significant influence of these parameters on Pd solubility in the haplobasaltic fluid melt.

At 1200°C, Pd solubility decreases from 52.4 to 2.4 ppm (Figs. 1, 2) with decreasing f_{O_2} from HM to IW buffers. The equation of solubility of PGM oxides in a silicate melt is as follows:

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Dependence of Pd solubility in the DAA melt on oxygen fugacity. $T = 1200°C$, $P = 2$ kbar

Sample no.	Buffer	x_{H_2}	$-\log f_{O_2}$	f_{H_2O}, bar	Pd, ppm
Pd-86*	HM	$2.12 \cdot 10^{-5}$	2.58	2039	52.420
Pd-84*	HM	$2.12 \cdot 10^{-5}$	2.58	2039	50.957
Pd-90	RRO	$1.04 \cdot 10^{-3}$	5.96	2037	30.205
Pd-89	NNO	0.007	7.67	2025	22.936
Pd-94	–	0.05	9.30	1938	19.327
Pd-98	–	0.1	10.02	1836	19.718
Pd-95*	–	0.2	10.72	1632	13.562
Pd-99*	–	0.2	10.72	1632	10.602
Pd-82*	–	0.35	11.39	1325	8.251
Pd-85*	–	0.35	11.39	1325	6.624
Pd-81	–	0.50	11.86	1019	2.401
Pd-141**	HM	$2.31 \cdot 10^{-5}$	1.48	2027	320.273

Note: (*) Double runs; (**) $T = 1300°C$, $P = 2$ kbar.

$$M(metal) + (m/4)O_2 = MOm/2 \text{ (melt)} \qquad (1)$$

(hereinafter, m is the efficient valence of PGM in silicate melt). Hence, one can draw two important conclusions: the Pd solubility versus f_{O_2} relationship found in our experiments indicates its dissolution in the ionic rather than zero-valent form; and the angular coefficient k—the tangent of slope in the linear dependence $\log C_{Pd} - \log f_{O_2}$—must be equal to $m/4$. Hence, the effective PGM valence equals $4m$.

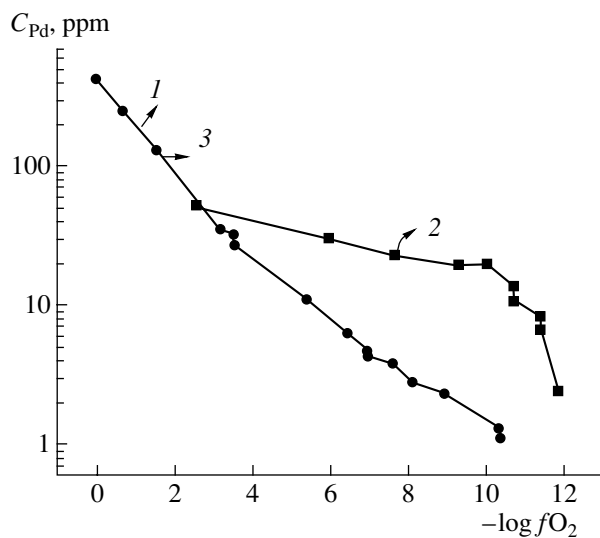In the $\log C_{Pd} - \log f_{O_2}$ diagram, the curve of Pd solubility in the melt versus f_{O_2} relationship is split into the oxidizing (f_{O_2} from HM to MW buffers) and reducing ($f_{O_2} \leq$ MW buffer) zones. In the oxidizing zone, a positive correlation between logPd solubility and $\log f_{O_2}$ is described by the equation

$$\log C_{Pd} \text{ (ppm)} = 1.876 + 0.065 \log f_{O_2} \qquad (2)$$

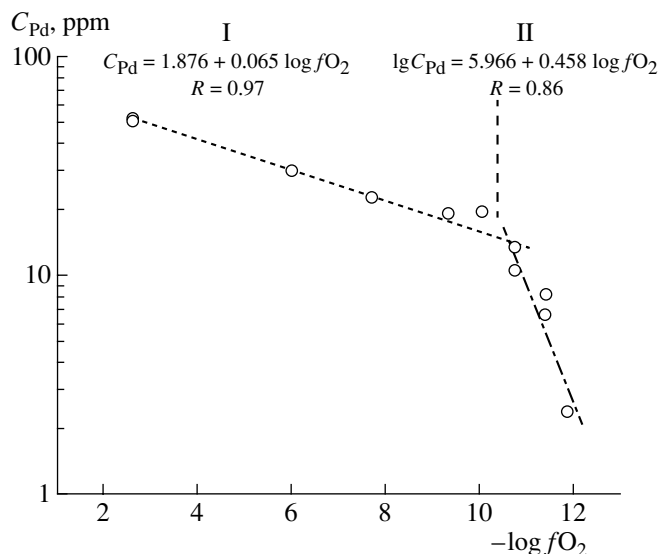with the angular coefficient equal to 0.065, which corresponds to an effective valence of Pd equal to 1/3.

Fig. 1. Dependence of Pd solubility on oxygen fugacity in the haplobasaltic melt. Our data: (*1*) $T = 1200°C$, (*2*) 1300°C; $P = 2$ kbar. (*3*) Data of Borisov *et al.* [8]: $T = 1350°C$, P = 1 atm.

Fig. 2. Dependence of Pd solubility on oxygen fugacity in the haplobasaltic melt. $T = 1200°C$, $P = 2$ kbar. Regression equations of $\log C_{Pd}$ dependence on $\log f_{O_2}$: (I) under oxidizing conditions with f_{O_2} ranging from HM to NNO buffer; (II) under reducing conditions at $f_{O_2} <$ NNO buffer.

At $f_{O_2} \leq$ MW buffer, the $\log C_{Pd} - \log f_{O_2}$ curve shows a break, and the positive correlation

$$\log C_{Pd} \text{ (ppm)} = 5.966 + 0.458 \log f_{O_2} \qquad (3)$$

is retained with a steeper slope and an angular coefficient equal to 0.46, indicating an effective valence of Pd of 5/3.

At high water fluid pressure, PGM can dissolve as hydroxides:

$$M(\text{metal}) + m/4 \ O_2 + m/2 \ H_2O$$
$$= M(OH)m/2(\text{melt}). \qquad (4)$$
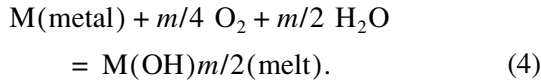
It is seen from Eq. (4) that PGM solubility depends not only on f_{O_2}, but also on f_{H_2O}.

Figure 3 demonstrates the dependence of Pd solubility on f_{H_2O}. Under oxidizing conditions within f_{O_2} from HM to NNO buffer, water fugacity decreases insignificantly (from 2039 to 2035), f_{O_2} decreases from –2.58 to –7.67 log units, while Pd solubility decreases from 52 to 23 ppm. This indicates that the decrease of Pd solubility is mainly caused by a change in f_{O_2}.

At $f_{O_2} \leq$ NNO, $\log C_{Pd}$ shows a positive correlation with $\log f_{H_2O}$ according to the equation

$$\log C_{Pd} \text{ (ppm)} = -8.982 + 3.136 \log f_{H_2O}. \qquad (5)$$

Under oxidizing conditions of HM buffer, Pd solubility in the water-saturated ($P = 2$ kbar) and aqueous fluid-free "dry" ($P = 1$ atm) haplobasaltic melts is similar. During the subsequent decrease in f_{O_2}, the Pd solubility in the water-bearing melt decreases much more slowly than in the dry melt (Fig. 1). Equation (4) suggests that these differences can be explained by the influence of not only f_{O_2} but also f_{H_2O} on the solubility. Since $\log f_{H_2O} > 0$ at a water–hydrogen fluid pressure of 2 kbar, when f_{O_2} changes, the Pd solubility in the water-bearing melt increases by $m/2 \log f_{H_2O}$ as compared to that in dry melts. For the same reason, PGM solubility decreases less rapidly with the decrease of f_{O_2}, while angular coefficient, i.e., slope of the $\log C_{Pd} - \log f_{O_2}$ dependence, is smaller than in the dry melts.

The dependence of PGM solubility on the water content in water-bearing silicate melts is demonstrated by experimental data (Blaine *et al.*, 2005). These authors showed that Pt solubility in the haplobasaltic melt at 1250°C, water fluid pressure of 2 kbar, and f_{O_2} within HM–NNO buffers directly correlates with water content in the melt.
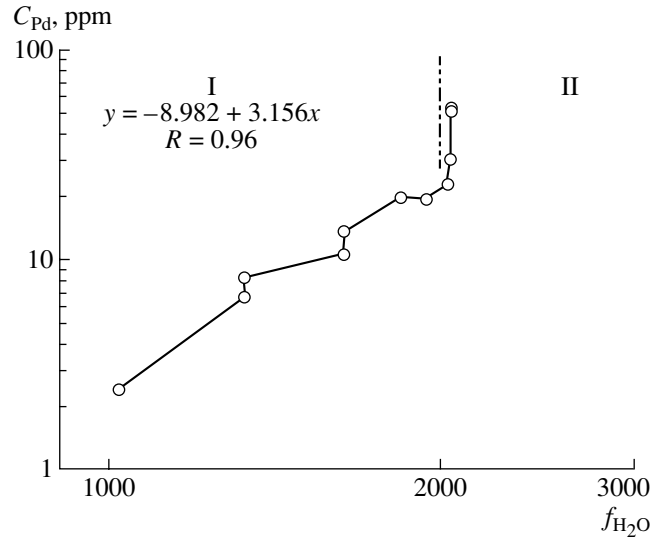
C_{Pd}, ppm

Fig. 3. Dependence of Pd solubility on water fugacity in the haplobasaltic melt. $T = 1200$°C, $P = 2$ kbar. Regression equation of $\log C_{Pd}$ on $\log f_{H_2O}$ is shown for reducing conditions at $f_{O_2} <$ NNO (sector I).

To describe the influence of the conjugate change of f_{O_2} and f_{H_2O} (since water and oxygen fugacities are linked by water decomposition reaction $H_2O = H_2 + \frac{1}{2}O_2$ on the Pd solubility, we can analyze the $\log C_{Pd} - \left[\frac{1}{2} \log f_{O_2} + \log f_{H_2O} \right]$ relationship following from Eq. (4):
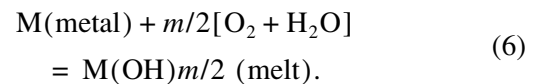
$$M(\text{metal}) + m/2[O_2 + H_2O]$$
$$= M(OH)m/2 \text{ (melt)}. \qquad (6)$$

Figure 4 shows the logarithmic dependence of Pd solubility on $\log \left[\frac{1}{2} \log f_{O_2} + \log f_{H_2O} \right]$, which takes into account the influence of oxygen and water on solubility. Taking into account f_{H_2O}, Pd solubility under oxidizing conditions is described by the equation

$$\log C_{Pd} \text{ (ppm)} = 1.460 + 0.119 \left[\frac{1}{2} \log f_{O_2} \right.$$
$$\left. + \log f_{H_2O} \right] \qquad (7)$$

with the angular coefficient 0.119 corresponding to an effective valence of 1/3 (as with the $\log C_{Pd} - \log f_{O_2}$ dependence).

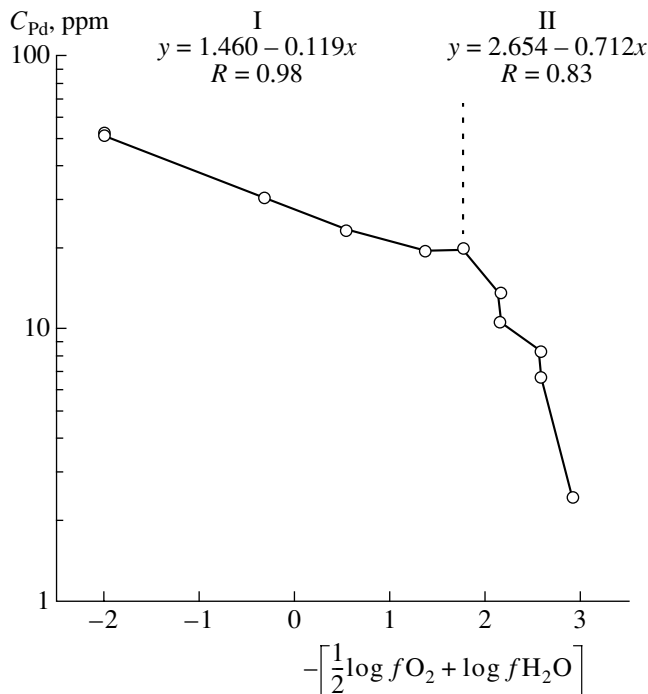Under reducing conditions, the Pd solubility in the water-bearing silicate melt is described by the equation

Fig. 4. Dependence of Pd solubility on oxygen and water fugacity in haplobasaltic melt. $T = 1200°C$, $P = 2$ kbar. Regression equation of $\log C_{Pd}$ on $\left[\frac{1}{2}\log f_{O_2} + \log f_{H_2O}\right]$ are shown for: (I) oxidizing conditions in the f_{O_2} range from HM to NNO buffers; (II) reducing conditions at $f_{O_2} <$ NNO buffer.

$$\log Pd \text{ (ppm)} = 2.654 + 0.712\left[\frac{1}{2}\log f_{O_2} \right.$$

$$\left. + \log f_{H_2O}\right] \qquad (8)$$

with the angular coefficient 0.712 corresponding to an effective valence of 3/2.

Thus, the aforementioned analysis of Pd solubility versus f_{O_2} and f_{H_2O} variations showed that the effective valence of Pd in the water-bearing haplobasaltic melt varies from 1/3 in oxidizing to 5/3 in the reducing conditions, which is significantly lower than 2 (the typical valent state of Pd in chemical compounds). Anomalous effective valences (below typical degree of oxidation in chemical compounds) calculated from the metal solubility in silicate melts versus oxygen fugacity relationships are also typical of other PGEs [1–3]. We propose two models to explain the peculiar fractional valence of Pd and other PGMs with a variation of f_{O_2} during dissolution in silicate melts. In the first model, melts can contain clusters (complexes) of charged and zero-valent particles that are responsible for a decrease

in effective valence. For example, an increase in effective valence from 1/3 to 5/3 with a change of f_{O_2} and f_{H_2O} from HM to IW buffer can be explained by the formation of (Pd^{1+} $2Pd^0$) clusters, which provide an effective valence of 1/3, and ($2Pd^{2+}$ Pd^{1+}) clusters, which provide an effective valence of 5/3. The second model assumes the simultaneous existence of three species in different valent states (Pd^{2+}, Pd^+, and Pd^0) in the melt, proportions of which vary with variations in f_{O_2}.

The study of the influence of temperature on the Pd solubility confirmed the previously detected anomalous temperature dependence of noble metal solubility in silicate melts [1–3]. With temperature increasing from 1200 to 1300°C at HM buffer and a water fluid pressure of 2 kbar, the Pd solubility in the haplobasaltic melt in our experiment increases from 51 to 320 ppm (table, Fig. 1). The sign of temperature dependence of Pd solubility differs from that in the well studied temperature dependence of the solubility of "normal" metals (in particular, Fe group elements) that are dissolved as ionic species and characterized by a decrease of solubility with increasing temperature. Such an anomalous temperature dependence of Pd solubility (and other PGMs) can be explained by the existence of Pd complexes (clusters) in the melt.

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