

PALLADIUM SOLUBILITY IN WATER-BEARING SILICATE MELTS: EVIDENCE FROM EXPERIMENTAL DATA

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Solubilities of Pd in silicate melts of a $\text{Di}_{55}\text{An}_{35}\text{Ab}_{10}$ (DAA) composition, close to eutectic Di-An, were conducted in the Pd capsules at 1200°C, fluid pressure of 2 kbar and $f\text{O}_2$ from HM to WI buffer. Hydrogen mole fraction varied from 0.05 to 0.50; $\lg f\text{O}_2$ 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 conducted in a vertically orientated internally heated gas high pressure vessel under conditions of known gas speciation and controlled fugacities. The duration of all experiments

was 72 hours. Glass samples were polished before analysis to remove possible contamination by the metal of the capsule. The oxygen fugacity was controlled by the double capsule buffer technique in oxidizing conditions (NM-NNO buffers) and by an Ar-H₂-gas mixture at reducing conditions ($\text{XH}_2 > 0.05$). Palladium concentrations were determined by instrumental neutron activation analysis (INNA).

At 1200°C Pd solubility decreases from 52.4 to 2.4 ppm with decreasing $f\text{O}_2$ from HM to IW buffers. With temperature increasing from 1200 to 1300°C at HM buffer and a water fluid pressure of 2 kbar, the Pd solubility increases from 51 to

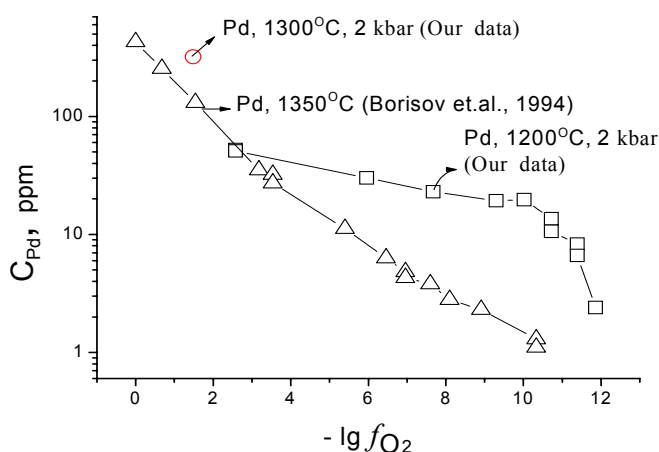


Fig. 1. Dependence of Pd solubility on oxygen fugacity.

320 ppm. At oxidizing conditions of HM buffer, Pd solubilities in the water-saturated ($P=2$ kbar) and free-water melts are similar (fig. 1). During the subsequent decrease in $f\text{O}_2$, the Pd solubility in the water-bearing melt decreases much more slowly than in the free-water melt. These differences can be explained by influence not only $f\text{O}_2$ but also $f\text{H}_2\text{O}$ on the solubility.

In the $\lg\text{CPd} - \lg f\text{O}_2$ diagram, the curve of Pd solubility in the melt versus $f\text{O}_2$ relationship is split into the oxidizing ($f\text{O}_2$ from HM to MW buffers) and reducing ($f\text{O}_2 \leq \text{MW buffer}$) zones. In the oxidizing zone a positive correlation between $\lg\text{CPd}$ and $\lg f\text{O}_2$ is described by the equation:

$$\lg\text{CPd (ppm)} = 1.876 + 0.065 \lg f\text{O}_2 \quad (1)$$

with the angular coefficient equal to 0.065, which corresponds to an effective valence of Pd equal to $1/4$. At $f\text{O}_2 \leq \text{MW buffer}$, the $\lg\text{CPd} - \lg f\text{O}_2$ is described by the equation:

$$\lg\text{CPd (ppm)} = 5.832 + 0.445 \lg f\text{O}_2 \quad (2)$$

with the angular coefficient equal to 0.445, which corresponds to an effective valence of Pd equal to $5/3$.

The dependence of $\lg\text{CPd}$ on $\lg f\text{O}_2$ indicates a change in valence of the dominant Pd species in the silicate melt. The data can be explained by the presences of complexes containing Pd^{2+} and Pd^0 that are responsible for a decrease in effective valence. The second model assumes the simultaneous existence of three species in different valent states (Pd^{2+} , Pd^{1+} and Pd^0) in the melt, proportions of which varies with variations in $f\text{O}_2$.

Fig. 2 demonstrates the dependence of Pd solubility on water fugacity. At oxidizing conditions within $f\text{O}_2$ from HM to NNO buffer, water fugacity decreases insignificantly (from 2039 to 2035), $f\text{O}_2$ 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 $f\text{O}_2$.

The solubility of Pd was also determined at 1300°C at the HM buffer to evaluate the temperature dependence of solubility. The Pd solubility increases with increase in temperature along HM buffer from 51 ppm at 1200°C to 320 ppm at 1300°C.

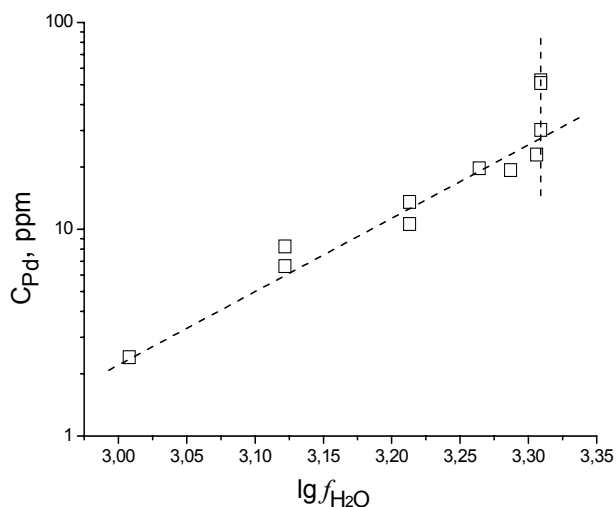


Fig. 2. Dependence of Pd solubility on water fugacity.
 $T=1200^{\circ}\text{C}$, $P=2\text{kbar}$.

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. The sign of temperature dependence of Pd solubility differs from that in the well studied temperature dependence of the solubility of “normal metals” (e.g. 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 can be explained by the existence of Pd complex (clusters) in the melt.

Reference

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