

SOLUBILITY OF RU AND PD IN SILICATE MELTS: THE EFFECT OF MELT COMPOSITION C. J. Capobianco¹ and R. L. Hervig² ¹Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721-0092; ²Center for Solid State Science, Arizona State University, Tempe, AZ 85287-1704

Solubilities of Ru and Pd in silicate melts having compositions in the Na₂O-MgO-CaO-Al₂O₃-TiO₂-SiO₂ ± FeO system were measured. Large changes in Ru solubility were correlated with the melt's ratio of non-bridging oxygens to tetrahedral cations, nbo/t. Ru wt% = (190)exp[-22000/T + 3.7 + 1.7(nbo/t)]. Palladium solubility showed negligible variation over the same compositional range. Thus, fractionation of Ru from Pd during magmatic differentiation could occur based simply on the difference in solubility as a function of melt basicity. We also found that substitution of FeO for MgO increases the solubility of Pd and Ru, but only slightly.

Introduction: Recent studies on the solubility of platinum group elements, PGE, in silicate melts have focused on the effect of oxygen fugacity while holding constant the melt composition, e.g., [1,2]. Moreover, to insure the constancy of composition as oxygen fugacity is varied most workers have found it experimentally convenient to exclude FeO (an important component of natural melts) from the simple silicate melts investigated. The variation of PGE solubility in those experiments allowed the valence of the dissolved species to be calculated. As discussed, for example, in [3] or [2] the valence of the dissolved melt species plays a critical role in defining the siderophile behavior of an element and its functional dependence on temperature and oxygen fugacity. Thus, these earlier experiments using constant compositions made the necessary first steps to interpreting the geochemistry of these noble elements.

A primary conclusion of previous work is that the oxidation states of noble metal species dissolved in the melt are unusually low, and do not correspond to the valences found in their most stable simple compounds. This unusual PGE speciation in silicate melts coupled with their intrinsically low solubilities implies that suitable bonding environments are scarce in the melts studied. On the other hand, our work [4,5] has shown that several PGE, e.g., Ir and Ru, have large, i.e., wt%, solubilities in their common oxidation states in solid oxides at magmatic temperatures. Obviously, these phases do provide bonding environments to host the common PGE ions, in contrast to melts studied recently. Our question is: Can the composition of a silicate melt be varied to significantly change the solubility of PGE?

We report here on two melt compositional variables and their effect on the solubility of Ru and Pd: 1) melt basicity, characterized by nbo/t [6], where melts with larger nbo/t are, in a chemical sense, more oxide-like; and 2) Fe content, which was selected to address the common suspicion that siderophile elements can be melt-stabilized by other transition elements, in particular Fe.

Methods: Three primary compositions were used for these solubility studies: A) an acidic composition in the nepheline-forsterite-silica ternary; B) a basic composition in the diopside-"CaTiAl₂O₆" pseudo binary; and C) the eutectic composition in the diopside-anorthite-forsterite ternary.

To investigate the effect of melt basicity mixtures of glasses A and B were contained with RuO₂ in Au₇₅Pd₂₅ capsules that were welded shut to prevent volatile loss. Samples were run in Deltech furnaces at 1250, 1300, 1350 and 1400°C (in the highest temperature runs Pt capsules were used).

Experiments similar to above were run to examine the effect of Fe on Ru and Pd melt solubility. An Fe glass based on composition B was made in which Fe was substituted for Mg to give Fe/(Mg+Fe)=0.5. Ruthenium and Pd solubilities for Fe-free and Fe-bearing systems could then be compared directly.

To further examine the effect of Fe another series of Pd solubility experiments was made at lower oxygen fugacities substituting Fe for Mg in composition C. Palladium crucibles were used to melt these mixtures at 1300°C in a gas-mixing furnace flowing CO:CO₂ mixes. Runs were made at logfO₂=-2.9 and -5.0.

Run products were analyzed primarily by electron microprobe. Palladium concentrations in the experiments from the lowest oxygen fugacity were analyzed by ion microprobe.

Results: Melt Basicity Fig. 1 illustrates the remarkable difference between Ru and Pd with regard to their silicate melt solubility chemistry. Ruthenium, but not Pd, shows marked increases in solubility with increasing oxide-like character of the silicate melt. This parallels the difference in solid oxide solubility between Ru and Pd found in [5] and probably reflects a more strongly ionic character for Ru compared to Pd in these systems. These results suggest that basic melts may stabilize more ionic species.

Fig. 2 shows further characterization of the chemistry of Ru solubility in silicate melts. The

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parallel trends of the solubility data for the differing melt compositions indicate that the enthalpy of the dissolution reaction does not change with melt composition. This is consistent with a dissolution reaction in which reactant and product species do not change in character as melt composition is varied. The changing Ru solubility is then only a result of a changing proportion of reactant species, probably non-bridging oxygens.

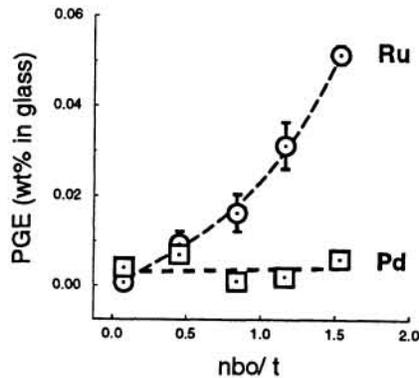


Figure 1. Solubility of Ru and Pd at 1250°C as a function melt basicity, nbo/t. Ruthenium (circles) and Pd (squares) show markedly different solubility behavior.

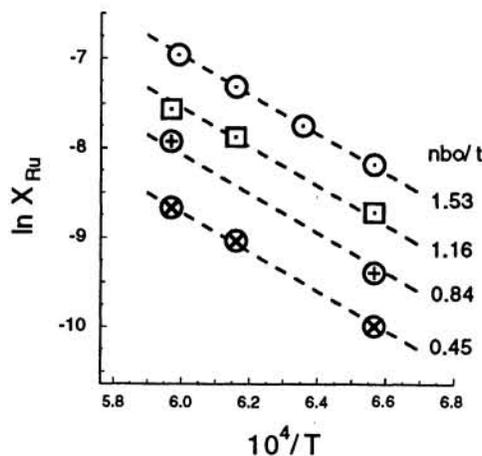


Figure 2. Logarithm of the mol fraction of Ru dissolved in silicate melt vs. inverse temperature. A different symbol is used for each silicate melt composition; the nbo/t ratios for these melts are also shown.

Effect of Fe We measured a 25-30% increase in solubility for Ru and Pd in our most basic melt when half the Mg was replaced by Fe, which produced a melt with 8 wt% Fe. This increase is minor, but

especially in comparison to the effect of melt basicity on Ru.

Further characterization of the effect of Fe on Pd solubility is shown in Fig. 3. At the lower oxygen fugacities of these runs our electron microprobe data are consistent, within the large error bars, with Pd solubility increases with Fe melt content. However in the lowest oxygen fugacity runs our ion probe data showed no change in Pd solubility between a melt with no Fe and one with 4 wt% Fe.

Moderate amounts of Fe in melts produce small increases in PGE solubility, and this is separate from the effect of melt basicity.

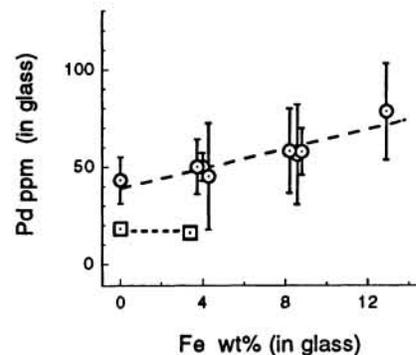


Figure 3. Palladium solubilities at 1300°C for Fe-substituted Di-An-Fo eutectic melts vs. Fe wt% in melt. Circles are for experiments run at $\log f_{O_2} = -2.9$ and were analyzed by electron microprobe; squares are for experiments run at $\log f_{O_2} = -5.0$ and were analyzed by ion probe.

Geochemical Implications: Melt basicity has a significant effect on the solubility of Ru, but not Pd. Therefore, as a magma evolves one may expect that Ru will be removed before Pd leading to larger Pd/Ru ratios in later differentiates. Also, in partial melts of the mantle the degree of melting should correlate negatively with Pd/Ru ratios if the PGE contents are solubility controlled.

References: [1] Borisov *et al.* (1994) *Geochim. Cosmochim. Acta* **58**, 705-716; [2] O'Neill *et al.* *Chem. Geol.* (1995) **120**, 255-273; [3] Capobianco *et al.* (1993) *J. Geophys. Res.* **98**, 5433-5443; [4] Capobianco and Drake (1990) *Geochim. Cosmochim. Acta* **54**, 869-874; [5] Capobianco *et al.* (1994) *Chem. Geol.* **113**, 23-43; [6] Mysen (1988) *Structure and Properties of Silicate Melts* Elsevier

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