

Partitioning and solubility of PGEs in oxides and silicates

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Introduction

Platinum group elements (PGEs) are among the most siderophile in the cosmochemical inventory. By analogy with iron meteorites, the bulk of Earth's chondritic endowment of PGEs is thought to be enconcentrated in its metallic core. In spite of their siderophilic nature, however, PGEs in the mantle are at nearly 1% of their chondritic concentrations. This relative enrichment has provided for a significant, and as yet poorly understood igneous geochemistry for the PGEs. However, recent experimental efforts have increased our understanding of their magmatic chemistry (e.g. Fleet *et al.* 1991, Borisov *et al.*, 1994 or Peach *et al.*, in press). After metals, the next most favored phases for PGEs are sulfides. Stabilization of PGEs in metals and sulfides accounts for much of their geochemistry. However, not all magmatic systems are metal- or sulfide-saturated. What governs PGE geochemistry in the absence of these important phases must be their solubility and partitioning behavior in oxide and silicate phases. Moreover, the strength of PGE chalcophilicity and siderophilicity is in part bound to their silicate melt chemistry and can be weakened by compatibilities among lithophile phases. We report here some experimental results on PGEs in oxides and silicates and discuss factors relevant to their lithophile geochemistry.

Methods

Experiments on the lithophile geochemistry of PGEs are complicated by their low solubilities in crystalline and molten silicates. To measure PGE concentrations in experimentally produced charges using microprobe techniques, such as the electron microprobe, ion microprobe and PIXE microprobe, we have conducted experiments under conditions (high oxygen fugacity) that produce PGE concentrations (ppm range) significantly above natural levels (ppb range). If the chemical species of dissolved PGEs does not change between our experimental conditions and those relevant to natural systems then our partition coefficients will be directly applicable, otherwise, their applicability depends on special considerations discussed below.

Partitioning and solubility experiments for Ru, Rh and Pd have been conducted in 1 atm. furnaces between 1250°C and 1510°C. Bulk compositions in simple systems containing subsets of the following components: CaO, MgO, Al₂O₃, SiO₂, FeO, TiO₂ have been investigated in equilibrations lasting between 1 and 16 days, a typical run is 3–4 days. Ru, Pd and Rh, the light PGEs, were selected for study primarily because their solubilities are generally greater than the heavy PGEs: Os, Ir and Pt, and so they are more easily analyzed. However, we are also attempting solubility measurements of Ir in Fe oxides using piston

Table 1. Summary of some experimental results for crystal/melt partitioning of Ru, Rh and Pd

crystal/melt	T (°C)	log f_{O_2}	Ru	Rh	Pd
perovskite	1300	-0.68	400	10	-
sphene	1300	-0.68	12	1	-
rutile	1300	0	2000	-	-
magnetite ¹	1250–1280	-3.5	100–4000	100–400	0.4–1.2
spinel ²	1300–1450	-0.68–0	22–25	78–90	<0.02 ³
forsterite	1290–1510	0	0.8–0.2	12–1.8	<0.2 ³
diopside	1300	0	1.9	3	<0.3 ³
anorthite	1300	0	<0.3 ³	<0.4 ³	<0.2 ³

¹solid solution near 85% magnetite 15% spinel (see Capobianco *et al.* 1994); ²MgAl₂O₄ (see Capobianco and Drake, 1990); ³upper limit established from PGE melt concentration and detection limit for e⁻ probe analysis of crystal.

cylinder techniques in which samples are exposed to high oxygen fugacity.

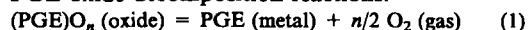
Results and Discussion

Table 1 reports Nernst crystal/melt partition coefficients for Ru, Rh and Pd for a variety of oxide and silicate crystals. The order of compatibility for the light PGEs is $Ru > Rh \gg Pd$. Pd is incompatible in all phases measured except magnetite to which it appears to be indifferent. This is in sharp contrast with Ru and Rh which exhibit a range of behavior from incompatible to extremely compatible. Differences in partitioning between Pd, on one hand, and Ru and Rh on the other are in part related to the differences in silicate melt solubilities probably reflecting different melt species between the two groups. Pd, although only sparingly soluble, is more soluble than either Ru or Rh under similar conditions of temperature and oxygen fugacity.

The range of partitioning behavior exhibited by Ru and Rh can be systematized by the type of crystal involved. Major differences in partitioning cleave on whether the crystal is an oxide or a silicate. Extreme compatibility is found for several non-silicates to the extent that measured concentrations in crystals of experimental charges are at wt.% levels indicating that true solid solution on major crystallographic sites is occurring. Such wt.% solid solution has been found for Rh in spinel, for Ru in magnetite, perovskite, and rutile and, from a preliminary high pressure synthesis, for Ir in magnetite.

Among crystalline silicates a rough correlation exists between compatibility of Ru or Rh and silicate polymerization in the crystal structure. For example, both elements are incompatible in anorthite and both are most compatible in an orthosilicates (spene for Ru and forsterite for Rh), while mildly compatible behavior is found for both elements in diopside, which is intermediate in silicate polymerization. However, there are conflicts in this simple picture, e.g., Ru is more compatible in forsterite than in diopside and Rh is more compatible in diopside than in spene. Obviously, more subtle crystal chemical influences are at work.

For partition coefficients of Table 1 to be directly applicable to magmatic conditions, where oxygen fugacities are much lower, hinges on the stabilities of the oxidized PGE species. We can gauge this stability from the thermodynamics of PGE oxide decomposition reactions:



From calculated equilibrium constants for these reactions the activities of PGE oxides can

be calculated for oxygen fugacities relevant to petrogenesis (e.g. QFM). If one assumes ideal mixing for the $(PGE)_nO_n$ component among the other oxide components, estimates for PGE concentrations can be calculated.

For Pd^{2+} , Ru^{4+} , Rh^{3+} , Os^{4+} , and Ir^{4+} calculated concentrations decrease respectively. However along the QFM buffer for temperatures above 1200°C the saturation concentrations are mostly well above typical natural levels, ranging from 10⁴ ppb for Pd to 1 ppb for Ir at 1200°C. Moreover, these concentrations far surpass estimates for silicate melt solubilities of the above PGE species under the same conditions and attest to their antipathy toward silicate bonding.

In fact, there is mounting evidence (e.g. Capobianco *et al.*, 1992; Borisov *et al.*, 1994) that dissolved PGE species in silicate melts have oxidation states that are unusually low and do not follow from expectations from stable pure PGE oxide phases. How does this affect the applicability of partition coefficients of Table 1? In general, it will tend to make the reported values too high because at magmatic oxygen fugacities the melt would be richer in PGEs than expected from the ionic equilibria governing under experimental conditions.

The moderate compatibility found for some of the silicate crystals could be leveled to indifference or even incompatibility by this effect, but the extreme and strong compatibility found for the oxide phases is unlikely to be completely erased. The important fact remains that the activities of the stable PGE oxides calculated from Eqn. 1 can exceed natural abundances under natural conditions. Thus, the unfavorable PGE chemistry in silicate melts which leads to the 'compromised' PGE species of unusually low valence state could be ameliorated by a redox reaction in the presence of a crystalline oxide host which could then harbor oxidized PGEs at levels perhaps comparable to natural abundances with only an insignificant change in a multivalent major element ratio.

References

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