

**CRYSTAL/MELT PARTITIONING OF RU, RH AND PD FOR SILICATE AND OXIDE BASALTIC LIQUIDUS PHASES.** Christopher J. Capobianco and Michael J. Drake, Lunar and Planetary Lab. University of Arizona, Tucson, AZ 85721, Pamela S. Z. Rogers, Los Alamos National Lab. Los Alamos, NM 87545

**Introduction:** The behavior the platinum group elements (PGEs) in mafic magmas (not saturated in metallic Fe or sulfide) may be governed by ionic trace element equilibria among typical basaltic silicate and oxide liquidus phases. To constrain the potential influence of lithophile crystal/melt fractionation on PGE distribution in igneous rocks we report some results from an experimental investigation of the crystal/melt partitioning behavior of Ru, Rh and Pd for forsterite, diopside, spinel, magnetite and anorthite. We have focussed on Ru, Rh and Pd because these elements are more soluble in the silicates and oxides under consideration than are the third series PGEs (Os, Ir and Pt) and so they are measurable in our experimental run products by microprobes of various sorts.

**Experimental Methods:** One atmosphere crystal/melt partitioning experiments were conducted in gas-mixing MoSi<sub>2</sub> element furnaces equipped with Pt-Pt/Rh thermocouples and zirconia solid electrolyte fO<sub>2</sub> sensors. Oxide mixes for experiments in the CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system were used directly in some experiments or they were pre-melted in their capsules using an oxy-acetylene torch prior to insertion into the furnaces. In Fe-bearing runs "FeO" was added as Fe metal and Fe<sub>2</sub>O<sub>3</sub> powders. PGEs were added to the charges as metals; foil (Pd), finely divided powder (Ru,) or wire (Rh). Rhodium was also added in some runs as Rh<sub>2</sub>O<sub>3</sub>. Several sample encapsulation methods were used for the reported experiments. Rhodium wire loops and Pd foil envelopes were used for most of the forsterite/melt partition coefficients. Synthetic mineral capsules made from single crystal spinel or polycrystalline anorthite were employed for Ru, Rh and Pd partitioning of anorthite/melt, spinel/melt and forsterite/melt experiments. Silica glass tubes were used for diopside/melt and spinel-magnetite/melt partitioning experiments. In some Fe-bearing runs the silica tubes were evacuated, and self-buffered otherwise the tubes were open and the fO<sub>2</sub> was set by CO<sub>2</sub>/H<sub>2</sub> mixtures. Run durations varied between 2 days for the highest temperature runs and 2 weeks with a typical run duration of 5-7 days. Runs were quenched by withdrawal from the furnace.

Chemical analyses of run products were made using microprobe techniques. Major element compositions of coexisting phases were obtained from the University of Arizona Cameca SX50 electron microprobe. Ruthenium, Rh and Pd concentrations for crystals and melts were, in most cases, measured with the UA SX50 using PGE metals and alloys for standards. Long count times (up to 600 secs) at high beam currents (100-150 namps) allowed minimum detection concentrations (the WDS x-ray peak was accepted as indicating a PGE concentration if it was larger than 3 times counting statistics) near 50 ppm. For a significant number of analyses where concentrations were lower than 50 ppm the PIXE microprobe ( $\mu$ -PIXE) at the Ion Beam Materials Lab at Los Alamos National Laboratory has been useful. The  $\mu$ -PIXE gave minimum detection limits around 1 ppm for a 3 MeV proton beam and count times between 20-60 mins. For one Ru sample and one Rh sample the Arizona State University ion probe (SIMS) yielded estimates of PGE melt concentrations between 1 and 4 ppm for both elements.

**Equilibrium Considerations:** All partition coefficients ( $D$  = weight concentration ratio of element in crystal and melt) reported in Table 1 represent synthesis runs. We do not yet report any trace element "reversal" experiments. We believe that these  $D$ 's must be fairly close to equilibrium values for two reasons; (i) the experiments are reproducible and the  $D$ 's are not influenced by variations in experimental methods, provided the same run conditions are finally produced; (ii) variations in run conditions produce thermodynamically predictable changes in  $D$ . For example, although PGE concentrations in experimental charges were not always uniform throughout the entire charge partition coefficients, calculated from adjacent mineral/melt pairs yielded very similar values. Figure 1, a plot of Ru concentrations in diopside/melt couples, shows a linear dependence over a wide concentration range suggesting that both equilibrium and Henry's Law are applicable. Figure 2, showing the temperature dependence of Rh and Ru forsterite/melt partitioning, provides another example of systematic behavior which suggests that equilibrium was obtained; positive slopes on these plots are expected while the differing slopes, as compared to Ni, Co and Mn, may be rationalized by differing substitution mechanisms in the crystal.

**Results and Discussion:** Table 1 shows widely ranging values for  $D$  which could lead to significant fractionation of PGEs in magmas. In general, both Ru and Rh are compatible in mafic crystals while Pd shows predominantly incompatible behavior. The strength of the compatibility

depends strongly on the particular crystalline phase and its composition. For instance, oxides of the spinel type show some very large D's but the order of magnitude is strongly dependent on the presence of Fe which even changes the order of compatibility for Ru and Rh. Compatibility of Rh and to a lesser extent Ru in forsterite and diopside is of particular interest because these are major phases in mafic magmas. The differences in compatibilities reported here and the chondritic relative proportions of the PGEs in the earth's mantle (Chou, 1978) suggest that the terrestrial upper mantle PGE pattern is not magmatically derived.

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**References:** Chou, C. -L. (1978) Proc. Lunar Planet. Sci. Conf. 9th, 219-230. Irving, A. J. (1978) Geochim. et Cosmochim. Acta, 42, 743-770.

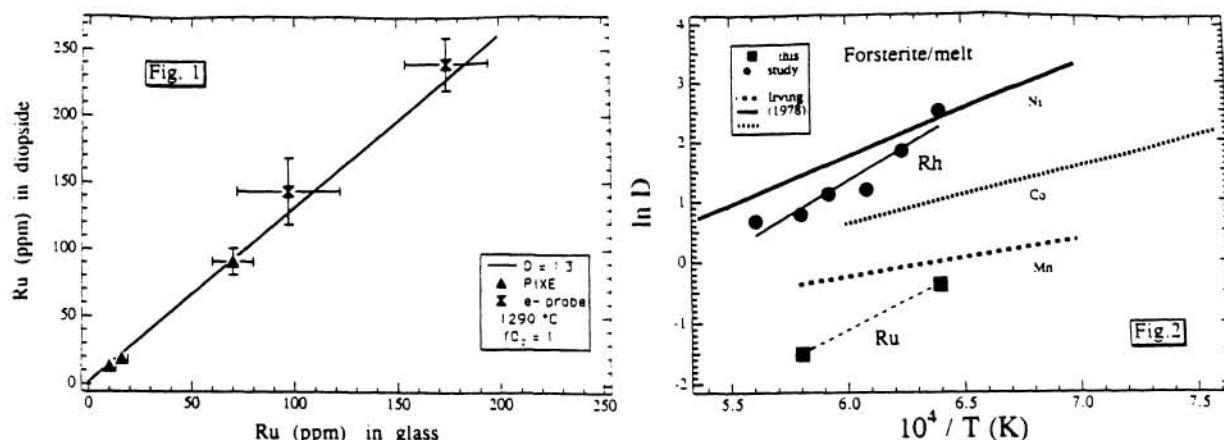


Table 1. Summary of some one atmosphere experimental results for crystal/melt partitioning of Ru, Rh and Pd.

phase/melt	T (°C)	log f <sub>O<sub>2</sub></sub>	Ru	Rh	Pd
spinel	1450	-0.68	25(9)*	78(15)	--
"	1450	0	--	--	<0.02
"	1290	-0.68	22(9)	--	--
"	1300	0	--	90(10)	--
magnetite	1250	-5 <sup>1</sup>	8000 <sup>2,3</sup>	300 <sup>2,3</sup>	0.8 <sup>2</sup>
"	1275	-3.3	>300 <sup>4</sup>	--	>4 <sup>4</sup>
anorthite	1300	0	<0.3 <sup>5</sup>	<0.4 <sup>5</sup>	<0.2 <sup>5</sup>
diopside	1300	0	1.9(.7)	3(1)	<0.3 <sup>5</sup>
forsterite	1290	0	0.8(.3)	12	--
"	1320	0	--	--	0.4 <sup>6</sup>
"	1330	0	--	6.3	--
"	1370	0	--	3.3	--
"	1415	0	--	3.1	--
"	1450	0	0.2(.1)	2.2	<0.2 <sup>5</sup>
"	1510	0	--	1.8	--

\*values in parentheses are one standard deviation of mean of reported D; <sup>1</sup>estimated from Fe contents of PGE metal and magnetite; <sup>2</sup>solid solution near 85% magnetite 15% spinel; <sup>3</sup>reported D based on SIMS-measured PGE concentration in glass near 1-3 ppm; <sup>4</sup>lower limit estimated using 50 ppm minimum detection for e<sup>-</sup> probe analysis of glass coexisting with pure magnetite; <sup>5</sup>upper limit estimated using 50 ppm minimum detection for e<sup>-</sup> probe analysis of crystal; <sup>6</sup>single determination requires confirmation