

INFLUENCE OF SILICATE MELT COMPOSITION ON METAL/SILICATE PARTITIONING OF W, Ge, Ga and Ni. S. J. Singletary¹, K. Domanik¹ and M. J. Drake¹, ¹Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, 85721 (jumper@lpl.arizona.edu, kdomanik@lpl.arizona.edu, m Drake@lpl.arizona.edu).

Introduction: The depletion of the siderophile elements in the Earth's upper mantle relative to the chondritic meteorites is a geochemical imprint of core segregation [1]. Therefore, metal/silicate partition coefficients ($D_{m/s}$) for siderophile elements are essential to investigations of core formation when used in conjunction with the pattern of elemental abundances in the Earth's mantle [2-4]. The partitioning of siderophile elements is controlled by temperature, pressure, oxygen fugacity, and by the compositions of the metal and silicate phases.

Several recent studies have shown the importance of silicate melt composition on the partitioning of siderophile elements between silicate and metallic liquids. It has been demonstrated that many elements display increased solubility in less polymerized (mafic) melts [5]. However, the importance of silicate melt composition was believed to be minor compared to the influence of oxygen fugacity until studies showed that melt composition is an important factor at high pressures and temperatures [6,7]. [8] found that melt composition is also important for partitioning of high valency siderophile elements. [9] conducted 1 atmosphere experiments, varying only silicate melt composition, to assess the importance of silicate melt composition for the partitioning of W, Co and Ga and found that the valence of the dissolving species plays an important role in determining the effect of composition on solubility. In this study, we extend the data set of [9] to higher pressures and investigate the role of silicate melt composition on the partitioning of the siderophile elements W, Ge, Ga and Ni between metallic and silicate liquid.

Experimental Procedure: Experiments were performed in the Experimental Geochemistry Laboratory at the University of Arizona utilizing a non-end loaded piston cylinder apparatus with a barium carbonate pressure medium. Starting materials were created by combining the mafic and silicic compositions of [9] with Fe powder (~25 wt% of the total mixture) to achieve metal saturation. Small amounts of W, Ge, GeO, Ga₂O₃ and NiO powder (<2 wt% each) were also added to the starting compositions. The experiments were contained in a graphite capsule and performed at temperatures of 1400 and 1500°C and pressure fixed at 1.5 GPa. Experimental run products were analyzed with the University of Arizona Cameca SX50 electron microprobe with four wavelength dispersive spectrometers and a PAP ZAF correction program.

Experimental results: All experiments saturated with silicate liquid and metal. The metal phase is present as round, homogeneous blebs indicating it was in a liquid state at run conditions. The presence of a metal phase also indicates that oxygen fugacity was below the IW buffer. Two experiments also contain a gallium-rich spinel as an additional saturating phase. The more mafic experiments invariably contain abundant quench-growth crystals in the liquid (predominantly (Fe,Mg)O) that hindered microprobe analysis (Figure 1). Several steps were taken to obtain quench crystal free glass, including a set of experiments at higher temperature (1500°C) and pressure-quenching [10].

However, these steps did not yield crystal free glass.

Ni. Ni displays an essentially flat slope (0.09) within the error of our analysis, with $D_{Ni}^{m/s} = 1000$ at $nbo/t = 2.97$ and $D_{Ni}^{m/s} = 1000$ at $nbo/t = 1.10$. The slope of the best fit line is nearly identical to the one found by [8] for Co^{2+} (Figure 2).

W. We find that W is incompatible over the range of compositions used in this study with the exception of one Ni-free experiment with nbo/t of 1.48 ($D_W^{m/s} = 14$). A duplicate set of Ni-free experiments was conducted because of analysis interferences between nickel and tungsten. Tungsten displays a systematic behavior of increasing compatibility as melts become more silicic, with $D_W^{m/s} = 0.0005$ at $nbo/t = 2.97$ and $D_W^{m/s} = 0.09$ at $nbo/t = 1.1$. The slope of the best fit line for the Ni-free W data in nbo/t vs. $\log D$ space is -1.22 and close to the value of -1.34 found by [9] and indicates that W is present in the 4+ valence.

Experiments with no Ni present yield systematically higher partition values for W (see Table 1) with $D_W^{m/s} = 0.13$ at nbo/t of 2.83 and $D_W^{m/s} = 14$ at nbo/t of 1.48. These values are an order of magnitude larger than the Ni-bearing values at similar nbo/t values. The slope of the best fit line is similar to the Ni-bearing experiments (-1.6 vs. -1.2). Why this discrepancy exists is not understood at this time but further experiments are in progress to verify the numbers and resolve the issue.

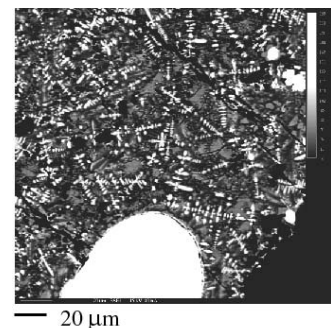


Figure 1. BSE image of a mafic end-member experiment displaying the nature of the metal/silicate contact and the quenched silicate liquid.

Ge. Partition coefficient values for Ge between metallic and silicate liquid range from 11 at nbo/t of 2.83 to 240 at nbo/t value of 1.52. Of the eight experiments in the set, two were run with Ge added to the mix as GeO₂. These two experiments display much lower $D_{Ge}^{m/s}$ values (0.12 at nbo/t of 2.75 and 2.5 at nbo/t of 1.48). The reason for this discrepancy is not known, but it may be due to lack of equilibrium. Further experiments are in progress to resolve this problem. The slopes of the Ge and GeO₂ doped experiments in logD_(m/s)-nbo/t space are similar (-0.67 and -1.05) indicating that Ge becomes more lithophile in very mafic melts but remains compatible in the metal (with the exception of one GeO₂ doped experiment). These values plot well above where predicted in a plot of slope vs. valence (Figure 2). No observable differences were noted between the Ni and Ni-free experiments.

Ga. Gallium behaves as an incompatible element over the range of experiments with the exception of two experiments. Two experiments that were also doped with GeO₂ yield $D_{Ga}^{m/s}$ values that are systematically higher than experiments doped with Ge powder. In these two experiments, Ga behaves as a compatible element with $D_{Ga}^{m/s} = 8.4$ at nbo/t of 2.75 and $D_{Ga}^{m/s} = 5.7$ at nbo/t of 1.48. In experiments doped with Ge powder, Ga displays a slightly negative slope (-0.14) with $D_{Ga}^{m/s} = 0.10$ at nbo/t = 2.97 and $D_{Ga}^{m/s} = 0.03$ at nbo/t = 1.1. The slope value plots closer to that found by [9] but is still above what would be predicted.

Conclusions: In general we find the same dependence of slope of data in nbo/t vs. logD_M against oxidation state at 1.5 GPa as found by [9] at 1 bar. We are conducting further experiments to assess whether failure to achieve equilibrium and/or non-ideal thermodynamic effects can account for apparently aberrant W and Ga results.

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Exp #	nbo/t	log D _{Ge}	log D _{Ga}	log D _W	log D _{Ni}
PM-8	1.10	2.1	-1.6	-1.0	3.0
PM-10	1.52	2.4	-1.2	-1.6	3.0
PM-7	2.40	1.2	-1.1	-2.7	3.4
PM-9	2.97	1.3	-1.0	-3.3	3.0
<i>PM-19</i>	<i>1.48</i>	<i>0.4</i>	<i>0.8</i>	<i>1.2</i>	-
<i>PM-20</i>	<i>2.75</i>	<i>-0.9</i>	<i>0.9</i>	<i>-1.6</i>	-
PM-15	2.76	1.1	-2.4	-0.5	-
PM-18	2.83	1.1	-1.9	-0.9	-

GeO doped experiments

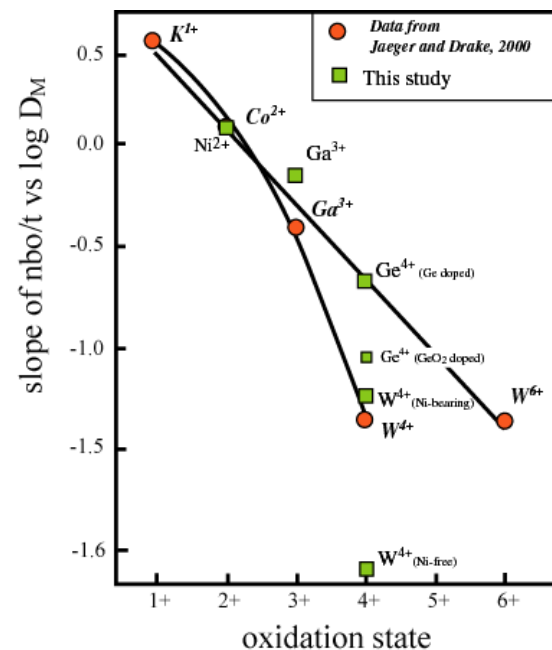


Figure 2. Slope of nbo/t vs Log D_{M/S} plotted against valence