THE PARTITIONING OF CO AND NI IN A SIMPLE METAL/SILICATE SYSTEM AS A FUNCTION OF OXYGEN FUGACITY AND TEMPERATURE

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Introduction: Several recent studies have inferred unusual chemistry for Ni and/or Co dissolved in silicate melts. Schmitt et al. (1989) reported 1+ valences for these elements based on the systematics of metal/silicate partitioning as a function of oxygen fugacity, but they attributed the unusual behavior to changes in silicate melt composition as the oxygen fugacity was varied. The work of Ehlers and Grove (1990), Colson (1990) and Steele et al. (1991) suggest that Ni in a zero valence state exists in silicate melts at measurable concentrations and becomes the majority species somewhere below iron-wüstite above 1400°C. These novel results impinge on recent efforts to characterize the metal/silicate partitioning of siderophile elements at the very high temperatures relevant to a terrestrial magma ocean (Murthy, 1991; Jones et al., 1991). To predict partitioning at conditions outside the range of measurement it is helpful to understand the governing chemical reactions. Since higher temperatures are more reducing, a very hot magma should have lower concentrations of oxidized species than a cooler magma at the same oxygen fugacity. To assess magma-oceanic concentrations of siderophile elements in equilibrium with core-forming metallic phases one should consider the chemistry of all dissolved species, not just the oxidized ones. We have therefore made a series of metal/silicate partitioning experiments for Ni and Co in a simple silicate melt in equilibrium with Pt. Here we were interested to 1.) confirm the unusual "metallic vapor" solubility in a silicate melt and 2.) to assess the temperature dependence of metal/silicate partitioning for Co and Ni.

Experimental Considerations: The base composition of the silicate melt was at the ternary eutectic in the diopside-anorthite-forsterite system. To this oxide mix eight starting compositions were prepared containing 18, 3.0, 1.5 or 0.75 wt.% NiO or CoO. Small beads (1mm diameter) of each of the above composition glasses were fused onto Pt quench wire loops. Equilibrations of the silicate melt and Pt quench wire were carried out at 1300°C, 1425°C and 1550°C in a vertical tube furnace equipped for gas-mixing. The oxygen fugacity set by H₂-CO₂ mixtures was measured with stabilized-ZrO₂ probes which were calibrated against IW, NNO and air. Run durations depended on temperature, the shortest, 4-5 hrs., at 1550°C and the longest, 23-27 hrs., at 1300°C. Platinum as a host metal for Ni and Co has the advantage of stability over a wide range of oxygen fugacity so that unusual behavior at low oxygen fugacity should be readily discernible as a deviation from well-defined trends extending over many orders of magnitude. Additionally, Pt does not appreciably dissolve in silicate melts so that the base glass composition does not change from run to run as it would if less noble metals were used.

Analytical Considerations: All charges were analyzed by a Cameca SX-50 electron microprobe. To analyze the low concentrations of Ni and Co a 15kV beam at 150namp was used and peak counts typically at 300secs. At the lowest concentrations (i.e. below 50 ppm) count times were extended to 600secs. Since metal at the lowest oxygen fugacities contained high concentrations of Ni or Co it was covered with Ag paint to avoid the possibility of counting x-rays not produced from within the glass. Traverses across samples toward or away from the metal did not show significant trends in concentration, but further analyses are still required to confirm homogeneity in all samples.

Results and Discussion: Figures 1 and 2 plot the log of metal/silicate partition coefficients, logDmet/sil, for Co and Ni, respectively, versus the log of the oxygen fugacity, logfO₂, for 1300, 1425, and 1550°C. The partition coefficient calculated is the activity of Ni or Co in the platinum (activity coefficients from Hultgren et al. 1973) divided by the cation mole fraction of Ni or Co in the glass. All the plotted points, except the lowest logfO₂ data points at each temperature, are averages of Dmet/sil obtained from equilibrations with varying total NiO and CoO. The error bars in these cases are 1 sigma from the mean. The standard wt. % ratio partition coefficients are not independent of total NiO or CoO because in many cases the metallic concentration is outside the Henry's Law range. The well-constrained errors in the activity-based partition coefficients are
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therefore a good indication that equilibrium was closely approached. For samples at the lowest logfO2 the error bars represent only the analytical error for singular composition experiments.

The curves plotted in Figures 1 and 2 are extrapolations from the highest logfO2 data points, i.e., those equilibrated in air. For these data, the temperature dependences of the equilibrium constants for the reactions below were obtained. Compared to the values of Robie et al. (1979) for the solid oxides of NiO and CoO our thermodynamic parameters are smaller due primarily to the effects of fusion and solution in the silicate.

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\begin{align*}
\text{NiO}_{\text{melt}} &= \text{Ni}_{\text{metal}} + \frac{1}{2} \text{O}_2 \\
\Delta H_0 &= 28.82 \pm 0.53 \text{ kcal/mol} \\
\Delta S_0 &= 10.04 \pm 0.32 \text{ cal/molK} \\
\text{CoO}_{\text{melt}} &= \text{Co}_{\text{metal}} + \frac{1}{2} \text{O}_2 \\
\Delta H_0 &= 32.10 \pm 1.79 \text{ kcal/mol} \\
\Delta S_0 &= 3.84 \pm 1.06 \text{ cal/molK}
\end{align*}
\]

Based on these preliminary data (we are examining our samples further) we find no significant deviation from the prediction of the simple oxidation/reduction equilibria represented in the above reactions. This appears to be so even for the runs at 1550°C which was run at the oxygen fugacity of iron-wüstite (IW) as well as the experiments at 1425°C and 1300°C run slightly below IW-1. Furthermore we find no evidence for the reduced oxidation state (1+) reported by Schmitt et al. (1989). One difference in technique between this work and Colson (1991) is the composition of the furnace gas. This study used CO2-H2 while Colson used CO2-CO.

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Figure 1. Metal/silicate partition coefficients for Co versus oxygen fugacity for three isothermal series at 1300, 1425 and 1550°C. Lines shown have been fit only to the data obtained in air. Deviations from this model curve are small and do not suggest participation of unusual valence states for Co.

Figure 2. Metal/silicate partition coefficients for Ni versus oxygen fugacity as in Figure 1. The unusual behavior reported by others for Ni has not been observed in this study.