PHASE EQUILIBRIA EFFECTS AND PARTITIONING OF NICKEL USING THE HUMPHREY COMPOSITION

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INTRODUCTION: The transition metals Fe, Mn, Co and Ni, as well as Mg, are fundamental to stabilizing high temperature phases in basalts. Ni is of particular interest because it is the most compatible of the divalent cations in basaltic systems. Numerous investigations [1-6] have documented partitioning behavior of these elements in an attempt to gain insight into early magmatic processes. From this body of work Jones' model [7] emerged, which was later revised [8] to account for newly published data and fO_2 effects. This study was undertaken to document the effect NiO has on phase stability and how Ni partitions in the initial stages of crystallization at high pressures and temperatures

Longhi and Walker [9] have recently utilized the revised D^{Ni}_{ol-liq} (D^{Ni}_{ol-liq}=Ni cation % ol. / Ni cation % liq.) model [8] to explain the seemingly inconsistent array of nickel concentrations found on the moon; although Ni is observed to act compatibly throughout natural magmatic systems, the more magnesium rich Mg-suite lunar rocks contain 250ppm less Ni than the more evolved (less Mg rich) low-Ti lunar mare basalts [9]. For a bottom-up crystallization sequence (3.0 GPa depth using a degassed upper mantle composition) of a lunar magma ocean, Longhi's MagFox/MagPox suite of programs predicts DNiol-liq values <1 (Ni enriched in melt over olivine) while Mg remains compatible during the first 10 % of crystallization when incorporating Jones [7] D^{Ni}_{ol-liq} model. Decoupling Ni from Mg (incompatible vs. compatible) would have profound implications for interpreting planetary Ni abundances and constraining conditions of core formation.

Initial experimental D^{Ni}_{ol-liq} values have matched those predicted, but the crucial early decoupling of Mg and Ni partitioning has not yet been duplicated.

Jones' model was calibrated using almost entirely terrestrial data. However, initial lunar olivine would have crystallized in a non-typical terrestrial system (i.e. devolitilized and Fe-Ni poor). Additionally, there is a lack of ultra-high temperature, near incompatible D^{Ni}_{ol-liq} data to validate the extrapolation of Jones [7] model into

lunar magma ocean conditions. We have tested Jones [7] model using a synthetic Martian basaltic composition in hopes of addressing the ability of the model to accurately predict near liquidus D^{Ni}_{ol-liq} values in planetary systems.

The Martian basalt, Humphrey, was chosen for this study because it has been well studied in the absence of Ni [10, 11]. This work provides a baseline to gauge what effect Ni has on phase stability. Because Ni is not commonly analyzed for in natural systems, its effects on phase stability are poorly understood and commonly overlooked. With a more complete understanding of Ni, its effects can better be compensated for in absence of complete chemical analysis.

METHOD: Our experiments were conducted at the Johnson Space Center High Pressure Laboratory using a piston cylinder press. A synthetic composition based on the Humphrey Basalt [12] plus NiO was made from a mix of oxides. This mix was fired at 1400° C and 1 atm to ensure minimal concentrations of H_2O. The fused mix was then ground and stored in a desiccator. Once loaded into graphite capsules our samples were stored for a minimum of 12 hours at 150° C. The experimental assembly consisted of $BaCO_3$ sleeves along with crushable MgO spacers. This assembly constrains fO_2 to QFM -1 to IW -1 [10, 13]. Temperature was measured using a W5Re/W25Re thermocouple. To ensure crystal-melt equilibrium samples were held at super liquidus conditions for 30 minutes before lowering to crystallization T where the sample equilibrated over 60 minute period. Major element analysis of our samples was completed using a Cameca SX-100 electron microprobe at the Johnson Space Center using synthetic oxides. Additionally, samples were analyzed for water content using a FTIR spectrometer. Analysis found 0.1 wt. % water, consistent with other work using the identical assemblies and similar compositions [10]. To ensure complete analysis of mineral assemblages and gauge mineral abundances, mass balance calculations were conducted using the least squares computations of IgPet software [16].

RESULTS: *Test of Jones' Model:* A series of experiments were run at temperatures ranging from 1300-1420° C and 8 to 14 kbar to obtain D^{Ni}_{ol-liq} values at near liquidus conditions. These data are

reported in Figure 1 along with Jones' D^{Ni}_{ol-liq} linear regression line. Equilibrium was checked by referencing experimental $D^{Fe}_{ol-liq}/D^{Mg}_{ol-liq}$ ratios to Jones' [14] published regression line. Experimentally determined D^{Fe}_{ol-liq} values are on average higher than Jones's values for a given D^{Mg}_{ol-liq} but are within 1 std. deviation and are consistent with published Martian basaltic data [10, 15].

Although D^{Ni}_{ol-liq} determined here for the Humphrey composition is always >>1, it does match predicted values by Jones' model. Additionally, as suggested by Jones [14], this correlation is independent of temperature and pressure.
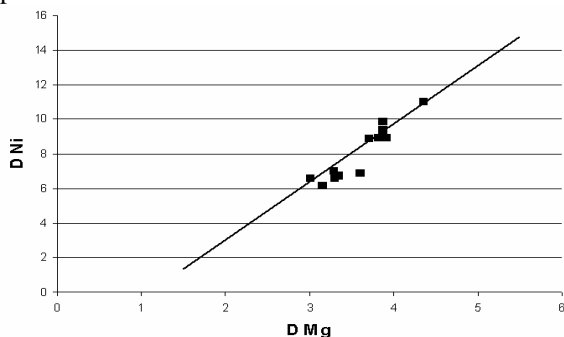

Figure 1: Humphrey $D^{Ni}_{ol-liq}/D^{Mg}_{ol-liq}$ plotted with a linear model (black line) [7, 14]

Effect on Phase Relations of Nickel: Phase assemblages in the experimental products include glass, olivine + glass and olivine + pigeonite + glass. The high pressure pigeonite + glass stability field is poorly constrained due to the absence of data in the 16 kbar region.
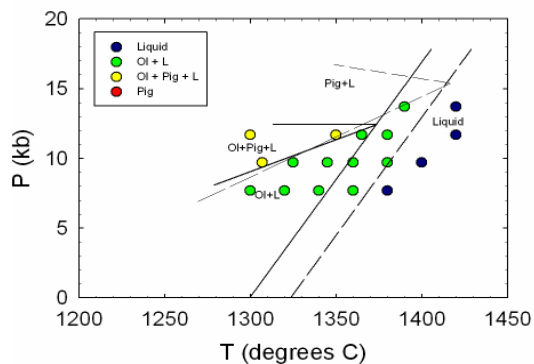

Figure 2: Phase Relations for Humphrey + Ni (dashed) compared with Humphrey Ni-free [10] (solid line).

The implied multiple saturation point is shifted 3 kbar higher (15.5 kbar) when compared to a Ni free system [10] as a result of the higher temperature liquidus and the unaltered slope of the pigeonite-in line.

DISCUSSION: *Test of Jones' Model:* The behavior of nickel in the Humphrey + NiO system supports the previous model [7, 14]. Although D^{Ni}_{ol-liq} values gathered in this study do not address the validity of extrapolating this model into to ultra-mafic systems, the independence of the model from temperature and pressure effects indicate extrapolation into initial lunar magma ocean pressures and temperatures may be valid. The success of the model in predicting D^{Ni}_{ol-liq} values in a Martian system provides evidence that the model can be applied to systems within other terrestrial bodies, such as the Moon.

Effect on Phase Relations of Nickel: The olivine saturated Humphrey + NiO liquidus is 25° C greater than that of Humphrey alone. The presence of Ni stabilizes olivine to higher temperatures than Mg and Fe alone due to its greater stability of Ni in olivine's crystal structure. This is evidenced by the higher average D^{Ni}_{ol-liq} value (8.30) compared to D^{Mg}_{ol-liq} (3.73), and by the greater heat of fusion of Ni olivine compared to Mg olivine (204 v. 113 kJ mol^{-1}) [8].

The addition of NiO did not, however, change the location of the pigeonite-in phase boundary [10]. This result is consistent with the near neutral partitioning of Ni and Mg into pigeonite ($D^{Ni}_{cpx-liq}/D^{Mg}_{cpx-liq}$=1.4). The unchanged pigeonite-in line leaves the higher pressure multiple saturation point (ol. + pig + melt) strictly as a function of the hotter liquidus. Further experiments at higher pressure will be needed to see how the pigeonite only liquidus curve is affected by NiO.

In summary, the addition of NiO to the Humphrey basalt forces olivine saturation to higher temperatures but pigeonite stability is basically unaffected.

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