

VARIATIONS ON A THEME BY LONGHI: I. AN ANALYSIS OF THE THERMODYNAMIC UNDERPINNING OF Fe, Mn, AND Ni PARTITIONING INTO OLIVINE. J.H. Jones, KR, NASA/JSC, Houston, TX. 77058 (john.h.jones@nasa.gov)

Longhi et al. [1] have used the $D(\text{Ni})$ vs. $D(\text{Mg})$ parameterizations of Jones [2, 3] in attempting to explain the Ni systematics of lunar differentiation. A key element of the Jones parameterization and the Longhi et al. models is that, at very high temperatures, Ni may become incompatible in olivine. Unfortunately, there is no actual experimental evidence that this is ever the case [1]. To date, all experiments designed to demonstrate such incompatibility have failed.

Here I will investigate the thermodynamic foundations of the D vs. $D(\text{Mg})$ trends for olivine/liquid discovered by [2]. The thermodynamic basis given by Jones [2] is seriously flawed because my analysis began with the assumption that

$$D = A/T + B \quad (1)$$

where D is the partition coefficient for some element between olivine and liquid, T is temperature, and A and B are constants. This faulty assumption can only be explained by Jones having had a very bad day. The correct starting point for any thermodynamic analysis should have been

$$\ln D = A/T + B \quad (2)$$

Progress has been made in this area, however. The following discussions will distinguish Ni from other elements partitioning into olivine.

Fe and Mn Partitioning. Linear parameterizations of $D(\text{Fe})$ and $D(\text{Mn})$ vs. $D(\text{Mg})$ can be simply explained because these regressions intersect the y-axis very near the origin. Therefore, the value of $D(\text{Fe})$ or $D(\text{Mn})$ can be approximated as zero when $D(\text{Mg})$ is zero. This is not the case for $D(\text{Ni})$, whose y-intercept is approximately -3.6.

Differentiating Eq. (2) by $1/T$ gives

$$\partial \ln D / \partial (1/T) = A \quad (3)$$

And in the Jones ([2] and Jones and Burnett [4] discussions of trace element partitioning, A is essentially equated with the heat of fusion of the mineral component of interest, i.e., fayalite, bunsenite, etc.

Despite my several failed attempts to describe the D vs. $D(\text{Mg})$ trends, the thermodynamic analysis of those trends for Fe and Mn is quite simple. Consider a superposition of $\partial \ln D(\text{Fe}) / \partial (1/T)$ [for example] and $\partial \ln D(\text{Mg}) / \partial (1/T)$ giving

$$[\partial \ln D(\text{Fe}) / \partial (1/T)] / [\partial \ln D(\text{Mg}) / \partial (1/T)] =$$

$$\partial \ln D(\text{Fe}) / \partial \ln D(\text{Mg}) = A(\text{Fe}) / A(\text{Mg}) \quad (4)$$

This can be expanded as

$$[\partial D(\text{Fe}) / D(\text{Fe})] / [\partial D(\text{Mg}) / D(\text{Mg})] = A(\text{Fe}) / A(\text{Mg}) \quad (5)$$

or

$$\partial D(\text{Fe}) / \partial D(\text{Mg}) = K_D(\text{Fe/Mg}) * A(\text{Fe}) / A(\text{Mg}) \quad (6)$$

A similar expression can be derived for $D(\text{Mn})$ vs. $D(\text{Mg})$. So the slopes of the Jones [2] regressions can today be calculated from known quantities: K_D 's for Fe/Mg and Mn/Mg and from heats of fusion (i.e., A 's). This calculation is only possible because the regressions for $D(\text{Fe})$ and $D(\text{Mn})$ vs. $D(\text{Mg})$ pass near the origin so that K_D is nearly constant.

Using heats of fusion for fayalite, bunsenite, and forsterite of 26.3 kcal/m, 32.5 kcal/m, and 27.2 kcal/mole [3], respectively, and $K_D(\text{Fe/Mg})$ and $K_D(\text{Mn/Mg})$ of 0.30 and .25, slopes on $D(\text{Fe})$ and $D(\text{Mn})$ vs. $D(\text{Mg})$ are calculated to be .29 and 0.30. The regression of experimental data for $D(\text{Fe})$ and $D(\text{Mn})$ give values of 0.30 and 0.26, respectively, in good agreement with prediction. Essentially, because the heats of fusion of fayalite, bunsenite, and forsterite are similar, the slopes of the D vs. $D(\text{Mg})$ regressions should nearly equal the K_D of the exchange, as is observed.

Ni Partitioning. The situation for elements such as Ni, whose D vs. $D(\text{Mg})$ regressions do not pass near the origin is more complicated. A consequence of eq. (6) is that the slope of a $D(\text{Ni})$ vs. $D(\text{Mg})$ diagram should not be constant because $K_D(\text{Ni/Mg})$ is not constant. However, given that there are regions of $D(\text{Ni})$ vs. $D(\text{Mg})$ space that can be approximated as linear, I will use the approximation

$$D(\text{Ni}) = a D(\text{Mg}) + b \quad (7)$$

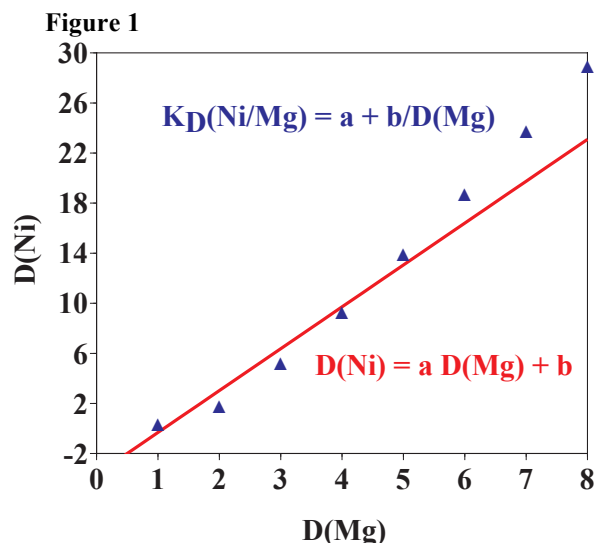
to find an approximate expression for $K_D(\text{Ni/Mg})$

$$K_D(\text{Ni/Mg}) = a + b/D(\text{Mg}) \quad (8)$$

where a and b are published regression coefficients [3], so that eq. (6) becomes, after integration from $D(\text{Mg})=1$ to $D(\text{Mg})$:

$$D(\text{Ni}) = \{a (D(\text{Mg}) - 1) + b \ln D(\text{Mg})\} A(\text{Ni}) / A(\text{Mg}) \quad (9)$$

Figure 1 compares the published regression of [3] to the functionality of eq. (9). Except at large values of $D(\text{Ni})$, the comparison is fairly good, especially considering that since eq. (8) is an approximation, eq. (9) must be as well. And, of course, no account has been taken for possible errors in the heats of fusion of the olivine components. Unlike the cases of $D(\text{Fe})$ and $D(\text{Mn})$, the $A(\text{i})/A(\text{Mg})$ term is not approximately unity, but is closer to a factor of two [3].



Can the functionality of eq. (9) fit real data? In Figure 2, I have regressed the combined data sets (L^3) of Longhi et al. [1] and Leeman and Lindstrom [5], using $D(\text{Mg})$ and $\ln D(\text{Mg})$ as the independent variables. The fit is quite good and is capable of explaining data at large values of $D(\text{Ni})$ that lie above the standard regression.

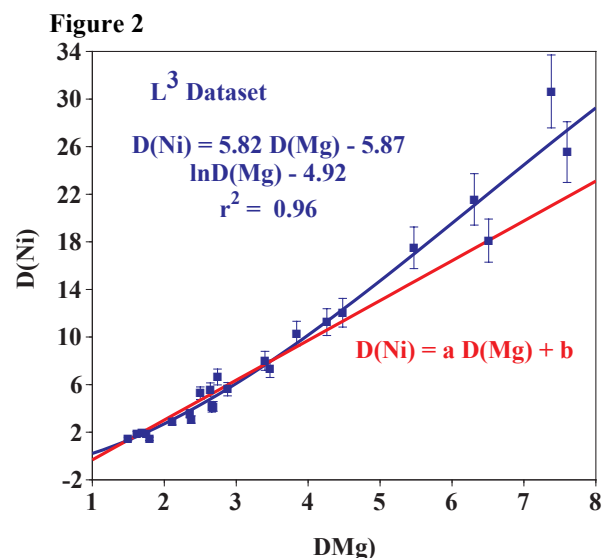
Discussion. I have used simple thermodynamic arguments and data to explain linear relationships between $D(\text{Fe})$, $D(\text{Mn})$, and $D(\text{Mg})$. The key to these relationships is the similarity of the heats of fusion of these olivine components. I have then shown that this same line of reasoning can be extended to $D(\text{Ni})$ vs. $D(\text{Mg})$ where differences in heats of fusion are large. However, this extension comes at the expense of a truly linear relationship. Nonetheless, an approximate functionality between $D(\text{Ni})$ and $D(\text{Mg})$ can be derived that serves to fit the experimental data.

An immediate question is how/why a non-linear relationship between $D(\text{Ni})$ and $D(\text{Mg})$ has been viewed as linear for so long. A large part of the reason is that the non-linearity really only expresses itself at high values of $D(\text{Ni})$ where errors are often large. Also in the original Jones (1984) paper, there were data points that fell both above and below the regression line.

With hindsight, though, it appears that the great majority of the points that fell below the regression came from a single study [6]. The reason for this is unclear. However, recent studies of $D(\text{Ni})$ for martian baalts [7, 8] also fall on the multi-regression given here. However, because these recent studies yielded intermediate values of $D(\text{Ni})$, they could equally well have been fit by the linear regression. Even so, it appears that the new regression is capable of describing $D(\text{Ni})$ in terrestrial, lunar and martian basalts.

It is also still unclear how $D(\text{Ni})$ will behave as $D(\text{Mg})$ approaches the origin. However, taking eq. (9) at face value, its second derivative is positive at $D(\text{Mg}) = 1$, implying that the function is concave down ("holds water"). This would also imply a flattening of the curve, relative to the standard linear regression. This flattening does not bode well for theories that postulate that Ni becomes incompatible in olivine at high temperatures.

Finally, the heat of fusion of Co-olivine predicts that it will behave more like Fe and Mn than Ni, and this appears to be the case. The y-intercept of the $D(\text{Co})$ vs. $D(\text{Mg})$ regression is much closer to the origin than that for $D(\text{Ni})$, although not quite as close as those for $D(\text{Fe})$ and $D(\text{Mn})$.



References: [1] Longhi J. et al. (2009) *GCA*, In press. [2] Jones J.H. (1984) *Cont. Min. Pet.* **88**, 126-132. [3] Beattie P. et al. (1991) *Cont. Min. Pet.* **109**, 212-224. [4] Jones J.H. and Burnett D.S. (1987) *GCA* **51**, 769-782. [5] Leeman W.P. and Linstrom D.J. (1978) *GCA* **42**, 801-816. [6] Takahashi E. (1978) *GCA* **42**, 1829-1844. [7] Filiberto J. et al. (2009) *Am. Min.* **94**, 256-261. [8] Herd C.D.K. et al. (2009) *Am. Min.* **94**, 244-255.