
Expressions of the form, \( \ln D(M) = a \ln fO2 + b/T + cP/T + d\ln(1-XS) + e(nbo/t) + f \), have been derived to predict \( D(M) \) (where \( D \) is a metal/silicate partition coefficient and \( M = \) Ni, Co, Mo, W and P) as a function of \( P, T, fO2 \), and silicate and metallic melt composition (\( nbo/t \) and \( XS \), respectively). Earth's upper mantle abundances of Ni, Co, Mo, W and P can be reconciled with simple metal-silicate equilibrium at \( P-T \) conditions near the upper/lower mantle interface (27 GPa, 2200 K, \( \Delta IW = -0.15, \ XS = 0.15 \) and \( nbo/t = 2.7 \)), in a magma ocean.

Introduction

Recent atmospheric models of the early Earth indicate that a thick, dense \( H_2O-CO_2 \) atmosphere developed during accretion [1,2]. The dense blanketing steam atmosphere caused surface heating to temperatures sufficient to melt the surface, and perhaps to depths of 1000 km [3,4]. If the Earth was molten to such depths, there may be geochemical or petrologic signatures retained by Earth's mantle of this early history. Although solid silicate/liquid silicate fractionation was most likely suppressed by turbulent convection in the molten mantle [2,5], metal/silicate equilibrium at depth may have left an imprint on the composition of the upper mantle, and more specifically on siderophile elements such as Ni, Co, Mo, W and P [6-8]. Until recently, there has not been sufficient metal-silicate partitioning data for these elements to allow quantitative modelling of their behavior as a function of \( P, T, fO2 \) and composition; however, recent partitioning determinations over a wide \( P-T-fO2-X \) range [9-12] provide data upon which to base prediction to upper/lower mantle \( P-T \) conditions. We will demonstrate in a later section that the abundances of Ni, Co, Mo, W and P in Earth's upper mantle are consistent with simple metal-silicate equilibrium at elevated pressure and temperature.

Effects of \( P, T, fO2 \) and silicate and metallic melt composition

Although the importance of temperature, metallic melt composition, and \( fO2 \) for metal-silicate partitioning of siderophile elements has been known for almost 15 years [e.g., 13-16], the effects of pressure and silicate melt composition have only recently been investigated. Several recent studies have determined that many partition coefficients decrease with increasing pressure [11,12,17]. Additional studies have revealed a silicate melt compositional effect whereby metal/silicate partition coefficients are lower for peridotitic than for basaltic melt systems [18-20]. These effects are taken into consideration in the predictive expressions developed below.

If one considers the following metal-silicate equilibria:

\[
M + x/4 O_2 = MO_{x/2}
\]

where \( -\Delta G'/RT = \ln K (K = aM^{n}O_{n/2}/(aM)^{n}(fO2)^{n/4}) \) (where "a" is the thermodynamic activity of the chemical species, "M" is Ni, Co, Mo, W or P, and "n" is the valence of M in the silicate liquid), then the partition coefficient, \( D(M) \) (\( D = C_{metal}^{M} / C_{sil,liq}^{M} \)), can be related to the free energy of the reaction. \( \ln D(M) \) can be related to \( T, P \) and \( fO2 \), by use of the following equation,

\[
\ln D(M) = a(T) + b/T + cP/T + f \]

where "a" is related to the valency of the metal oxide, and "b", "c" and "f" result from the expansion of the free energy term \( (\Delta G' = \Delta H' + T\Delta S' + PAV') \), and are related to \( \Delta H/RT, \Delta V'/R \) and \( \Delta S'/R \), respectively. Adding terms to account for the compositions of the metallic liquid (\( \ln(1-XS) \), see [16]) and silicate liquid (\( nbo/t \), see [21]) we have:

\[
\ln D(M) = a(T) + blnfO2 + cP/T + d\ln(1-XS) + e(nbo/t) + f \]

Partition coefficients measured (previous studies) at specific \( T, P, fO2 \) and composition can be used to derive constants "a" through "f" for each siderophile element by multiple linear regression (see Table 1).

Metal-silicate equilibrium near the upper mantle / lower mantle boundary

Assuming a chondritic bulk composition for the Earth, a core of 32% the mass of Earth consisting of 95% molten metal, and a totally molten mantle, the abundances of Ni, Co, Mo, W and P in the mantle can be calculated at specific \( P-T-fO2-X \) conditions for simple metal-silicate
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equilibrium. Using partitioning expressions developed for S-free systems, it is impossible to closely match Earth's upper mantle abundances [22] of these elements. Addition of S to the metallic liquid, however, allows a close match to Earth's upper mantle abundances, at 27 GPa, 2200 K, $\Delta W = -0.15$ (where $\Delta W$ refers to the oxygen fugacity relative to the iron-wustite buffer), nbo/t = 2.7 (peridotitic), and $X_S = 0.15$ (Fig. 1). This point in P-T space lies below the dry peridotite liquidus [23], but is likely to be near the liquidus in a hydrous peridotite [24].

This result suggests that a significant amount of water may have been dissolved in the early magma ocean. Our results also indicate that the upper mantle (molten peridotite) and lower mantle (perovskite-, magnesiowustite-, metal-bearing) may have been isolated early in Earth's history. The siderophile element abundances were set by liquid metal - liquid silicate equilibrium at the upper/lower mantle interface and subsequently imparted on the molten upper mantle by turbulent convection. This equilibrium condition was presumably set after the 'metal rainfall' predicted by Stevenson [25]. This result also suggests that the deep mantle could have held a significant amount of water, as the hydrous magma ocean crystallized. Many high pressure phases have water storage (e.g., viscosity, density, thermal conductivity, high pressure solubility in magma) before such a system can be quantitatively modeled. (Supported by NASA grant NAGW 3348)


<table>
<thead>
<tr>
<th>Table 1: Coefficients for InD expressions (S-bearing metallic liquid)</th>
<th>(units are Kelvins and gigapascals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td># pts.</td>
</tr>
<tr>
<td>Ni (LM/LS)</td>
<td>102</td>
</tr>
<tr>
<td>Co (LM/LS)</td>
<td>31</td>
</tr>
<tr>
<td>Mo (LM/LS)</td>
<td>22</td>
</tr>
<tr>
<td>W (LM/LS)</td>
<td>48</td>
</tr>
<tr>
<td>P (LM/LS)</td>
<td>16</td>
</tr>
</tbody>
</table>

Figure 1: comparison of mantle abundances of Ni, Co, Mo, W and P reported by McDonough and Sun (1995) with abundances calculated at 27 GPa, 2200K, $\Delta W = -0.15$, $X_S = 0.15$ and nbo/t = 2.7. Vertical error bars represent 2σ error on the calculated values, and horizontal error bars are uncertainties reported by McDonough and Sun (1995). The abundances of all five elements are consistent with metal-silicate equilibrium at high pressure conditions.