HIGH PRESSURE AND TEMPERATURE METAL-SILICATE PARTITIONING BEHAVIOR
OF MODERATELY SIDEROPHILE ELEMENTS: IMPLICATIONS FOR THE EARLY
HISTORY OF THE EARTH; Valerie J. Hillgren1, Michael J. Drake1, and David C. Rubie2.
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Introduction. It has been known for some time that siderophile element abundances in
the Earth's mantle are too high for metal to have been in equilibrium with silicate [e.g., 1],
particularly if equilibrium was established at low pressures and temperatures near the surface of
the accreting Earth. Although many hypotheses have been proposed to account for this apparent
disequilibrium, none has been entirely satisfactory [2]. Murthy [3] proposed that the problem
may be reconciled if metal-silicate equilibrium was established at high pressures and
temperatures. We have performed experiments on the distribution of siderophile elements
between liquid metal and liquid silicate at 100 kbars and 2000 °C. These experiments
demonstrate that it is unlikely that siderophile element abundances were established by simple
metal-silicate equilibrium at any combination of temperature and pressure, and that core
formation in the Earth was probably a mixture of complex physical and chemical processes.

Experimental Techniques. Experiments were conducted in the 1200 ton multianvil
apparatus at the Bayerisches Geoinstitut. The sample was contained in either MgO or Al2O3
capsules which were surrounded by a MgO sleeve contained within a cylindrical LaCrO3 heater
with a geometry designed to minimize thermal gradients across the sample [4]. The sample
assembly consisted of a MgO (+5 wt. % Cr2O3) octahedron with an edge length of 18 mm.
Temperature was monitored with a 0.25 mm diameter W3%Re/W25%Re thermocouple in
contact with the sample capsule.

The starting material consisted of a synthetic basalt prepared by mixing together reagent
grade oxides in the following proportions: 50 wt. % SiO2, 19 wt. % FeO, 13 wt. % Al2O3, 11
wt. % CaO, and 7 wt. % MgO. This synthetic basalt was doped with 1.5 wt. % each of NiO and
CoO, or MoO3 and WO3, or V2O5, Cr2O3, and MnO. These mixtures were melted and quenched
to a glass and then ground back to a powder. This glass powder and Fe metal filings were mixed
together in an approximately 50-50 ratio by mass.

The samples were first brought to a pressure of 100 kbars, and then were heated to 1600
°C and held at that temperature for 45-60 minutes to sinter the capsule material in order to
minimize its subsequent chemical interaction with the sample. The temperature was then raised
to 2000 °C and held there for 3 minutes. At this temperature and pressure, both metal and silicate
are liquids. The charges were quenched rapidly (to less than 300 °C in 1 second) by turning off
the power to the LaCrO3 furnace.

Experimental results. The samples were analyzed with a Cameca SX50 electron
microprobe. The initially homogeneously distributed metal filings had largely segregated into
a single spheroid in the center of the charge. The silicate liquid did not quench to a glass but
segregated into two phases with a dendritic texture. Thus to determine the composition of the
silicate liquid prior to quenching the electron beam was rastered over an area approximately 20
µm on a side, and 30 to 40 analyses were taken and averaged together. For the metal a point
beam was used. For major elements a beam current of 30 nanoamps and a counting time of 15
seconds were used. For the trace elements beam currents between 125 and 250 nanoamps and
counting times of up to 10 minutes were used.

The metal-silicate partition coefficients we determined for Ni, Co, Mo, W, Fe, V, Cr, and Mn
are shown in Table 1 along with their one sigma uncertainties and an estimated oxygen fugacity
relative to the iron-wüstite buffer. Molybdenum and W were both below analytic detection in the
silicate glass, thus lower limits for their metal/silicate partition coefficients are reported. Our
results for Ni and Fe agree well with those of Walker et al. [5].

Discussion. In Figure 1, we compare our partition coefficients that were approximately
1.6 log units below the iron-wüstite buffer to 1260 °C, 1 bar data that were in a similar redox
state. This Figure shows that the Ni and Co metal-silicate partition coefficients decrease with
increasing temperature and pressure. Although the W partition coefficient measured in this study is only a lower limit, it is larger than its lower temperature and pressure counterpart indicating that W becomes more siderophile with increasing temperature and pressure. This result is contrary to the prediction of [3]. The Mo partition coefficient is also a lower limit. It is presently unclear whether Mo becomes less siderophile or more siderophile with increasing temperature and pressure. Because of the large variability of the lower temperature and pressure V, Cr, and Mn data, it is difficult to say what trends are present.

Although we are working under the assumption that temperature has a stronger influence on partitioning behavior than pressure, with this limited data set, we can not say for certain which variable is more important. There is evidence that pressure may play a significant role in the partitioning of siderophile elements [6].

The partition coefficients reported above may be used to evaluate whether simple high temperature equilibrium between metal and silicate during accretion of and core formation in the Earth can account for the abundances of Ni, Co, W, Mo, V, Cr, and Mn in the upper mantle of the Earth. In particular, the approximately equal abundances of Ni, Co, and W constitute a powerful test. Simple mass balance between the core and the mantle of the Earth may be used to calculate what metal-silicate partition coefficients are necessary to produce the observed abundances of these elements in the mantle. Calculated metal-silicate partition coefficients are given in Table 1. To first order, mean core-mantle partition coefficients for Ni, Co, and W need to be 40 ± 5. Inspection of Figure 1 indicates that this condition is not satisfied in the pressure range of 1 bar to 100 kbars and temperature range of 1260 °C to 2000 °C. Extrapolation of these results to higher temperatures and pressures is very uncertain, but there is little evidence that the metal-silicate partition coefficients for Ni, Co and W will ever converge on a value of 40 ± 5 for Ni, Co, and W, especially if the trends observed in Figure 1 continue.

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Figure 1: Comparison of 1260 °C, 1 bar partition coefficients to the ones measured in this study. One bar data from [7] and [8].

<table>
<thead>
<tr>
<th>Expd</th>
<th>capsule material</th>
<th>ΔFW</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>W</th>
<th>Mo</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
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<tr>
<td>888</td>
<td>Al₂O₃</td>
<td>-1.6</td>
<td>6.2±0.2</td>
<td>135±15</td>
<td>60±3</td>
<td>*</td>
<td>*</td>
<td>*</td>
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<tr>
<td>891</td>
<td>MgO</td>
<td>-2.3</td>
<td>12±0.4</td>
<td>247±44</td>
<td>106±16</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
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<tr>
<td>895</td>
<td>Al₂O₃</td>
<td>-1.6</td>
<td>6.0±0.1</td>
<td>*</td>
<td>&gt;123</td>
<td>&gt;360</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
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<tr>
<td>912</td>
<td>Al₂O₃</td>
<td>-1.6</td>
<td>6.5±0.5</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>0.09±0.01</td>
<td>0.32±0.03</td>
<td>0.016±0.002</td>
<td></td>
</tr>
</tbody>
</table>

| D<sub>met/sil</sub> required for core/mantle equilibrium | 16 | 45 | 40 | 35 | 160 | 4 | 5 | 13 |

* = not present in charge