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THE EXPERIMENTAL PARTITIONING BEHAVIOR OF TUNGSTEN AND PHOSPHORUS: IMPLICATIONS FOR THE COMPOSITION AND FORMATION OF THE EARTH, MOON AND EUCRITE PARENT BODY

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THE EXPERIMENTAL PARTITIONING BEHAVIOR OF TUNGSTEN AND PHOSPHORUS: IMPLICATIONS FOR THE COMPOSITION AND FORMATION OF THE EARTH, MOON AND EUCRITe PARENT BODY

by

Horton Elwood Newsom

A Dissertation Submitted to the Faculty of the DEPARTMENT OF GEOSCIENCES In Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY In the Graduate College THE UNIVERSITY OF ARIZONA

1982
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Horton Elwood Newsom entitled THE EXPERIMENTAL PARTITIONING BEHAVIOR OF TUNGSTEN AND PHOSPHORUS: IMPLICATIONS FOR THE COMPOSITION AND FORMATION OF THE EARTH, MOON AND EUCRITe PARENT BODY

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Dissertation Director

Date
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SIGNED: Horton E. Newsom
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I also could not have completed this work without the invaluable encouragement and understanding of my wife Joan. Joan is my staunchest supporter, and from her I have learned much about perseverance and patience. She also deserves great thanks for reading and editing this dissertation. Because of Joan's love and inspiration I also dedicate this dissertation to her.
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ABSTRACT

The solid-metal/silicate-melt partition coefficient for W has been determined experimentally for the temperature and oxygen fugacity conditions at which eucritic basalts formed. The partition coefficient for W is $25 \pm 5$ at 1190°C and an oxygen fugacity of $10^{-13.4}$. The solid-metal/silicate-melt partition coefficient for P, $D(P)$, has been determined experimentally at 1190°C and 1300°C. The dependence of the partition coefficient on oxygen fugacity is consistent with a valence state of 5 for P in the silicate melt. The experimental partition coefficients are given by:

$$\log D(P) = -1.21 \log f_{O_2} - 15.95 \text{ at } 1190°C$$

$$\log D(P) = -1.53 \log f_{O_2} - 17.73 \text{ at } 1300°C$$

The partition coefficients may be used to interpret the depletion of W/La and P/La ratios in the Earth, Moon, and eucrites relative to Cl chondrites. The depletion of the W/La ratios in the eucrites may be explained by partitioning of W into 2% to 10% solid metal assuming equilibration and separation of the metal from the silicates at low degrees of partial melting of the silicates. The depletion of P/La ratios requires an additional 5% to 25% sulfur-bearing metallic liquid. The depletion of both P/La and W/La ratios in the Moon can be explained by partitioning of P and W into liquid metal during formation of a small lunar core by metal-silicate separation at low degrees of partial melting of the silicates. The W/La ratios in the Earth and Moon are
virtually indistinguishable, while P/La ratios differ by a factor of two. The concentrations of FeO also appear to be different. These observations are difficult to reconcile with the hypothesis of a terrestrial origin of the Moon following formation of the Earth's core, but are consistent with an independent formation of the Earth and Moon. In contrast to the Moon and eucrites, the depletion of P/La and W/La ratios in the Earth cannot be explained by an internally consistent model involving equilibrium between metal and silicate at low pressures.
CHAPTER 1

INTRODUCTION

The abundances of siderophile elements in samples from differentiated planetary bodies may be used as probes of Fe-metal abundances and of core formation processes. The P/La and W/La ratios in samples from the Earth, Moon and Eucrite Parent Body (EPB) are lower than the ratios in Cl chondrites (Wänke et al., 1973; Dreibus, Spettel and Wänke, 1976). The ordinary chondrites and Cl chondrites with widely varying metal contents and oxidation states have similar P/La and W/La ratios suggesting that nebular fractionations were unimportant. Therefore, assuming that P, W and La are refractory and incompatible, the lowering of P and W abundances relative to La in the Earth, Moon and eucrites are presumably due to separation of metal from silicate during planetary-scale igneous events.

The eucrites are basaltic achondrite meteorites which probably formed on an asteroidal-sized parent body (radius less than 500 km) shortly after the formation of the solar system. Knowledge of the chemical and mineralogical composition of the eucrite parent body (EPB) permits us to address several interesting questions such as (a) the homogeneity and internal structure of asteroidal-sized bodies, (b) the relationship between the basaltic meteorite parent bodies and the undifferentiated (chondritic) meteorites, and (c) the geochemical
behavior of chemical elements during basalt formation under conditions more reducing than are generally found on the Earth at present.

A reasonable agreement exists among different investigators regarding the silicate composition of the eucrite basalt source regions except for the amount of FeO in the silicate composition (Consolmagno and Drake, 1977; Morgan et al., 1978; Dreibus and Wänke, 1980). Estimates of the abundance and distribution of metal vary widely with reported metal contents of 13% ± 3-4% (Morgan et al., 1978), >20% (Dreibus and Wänke, 1980), and 37 ± 5% (Palme and Rammensee, 1981).

This dissertation reexamines the question of the abundance and distribution of metal in the EPB and addresses in Chapter 4 the question of the early igneous history of the EPB. Reported are metal/silicate-melt partition coefficients for P and W determined experimentally under conditions appropriate to eucrite petrogenesis. These data are utilized to examine metal-silicate fractionation in the EPB.

The abundances of siderophile elements in the Earth and Moon have also been the focus of recent controversy regarding the origin of the Moon (Delano and Ringwood, 1978; Anders, 1978). For the Moon, Rammensee and Wänke (1977) concluded that any geophysically reasonable metallic lunar core would be too small to explain the large lunar W/La depletion, and it was therefore suggested that the Moon acquired a low W/La ratio in a non-lunar igneous event. This conclusion was used to support the hypothesis that the Moon formed by fission from the proto-Earth, the upper portion of which was depleted in W due to terrestrial core formation (Rammensee and Wänke, 1977; Ringwood, 1979).
In Chapters 5 and 6 this conclusion is shown to be implicitly based on a special case, namely equilibrium between metal and silicate phases with total melting of silicates. In the geologically plausible case where metal fractionates from silicate at relatively low degrees of partial melting, the incompatible nature of W may disprove their conclusion. A metallic core that is geophysically plausible can account for the depletion of P and W in the lunar crust and, presumably, in the lunar mantle. Therefore, the low W/La and P/La ratios in the Moon can no longer be used as unconditional evidence for a terrestrial origin of the Moon.
CHAPTER 2

METAL–SILICATE PARTITIONING EXPERIMENTS

2.1 EXPERIMENTAL PROCEDURES

Metal/silicate-melt partitioning experiments for P and W were performed in a vertical muffle tube furnace equipped with a gas mixing apparatus. Oxygen fugacity in the experiments was controlled using mixtures of \( \text{H}_2 \) and \( \text{CO}_2 \), and was actively monitored with a system using a solid ceramic electrolyte oxygen concentration cell, modified after a design by Williams and Mullins (1976). The cell is schematically arranged as follows:

Reference \( f_0^2 \), M | Electrolyte for \( 0^-2 \) ions | M, Unknown \( f_0^2 \)

where M represents the platinium electrodes. The net reaction at the cell is:

\[
\text{O}_2 + 4\text{e}^- = 2\text{O}^-2
\]  

(2.1)

and the voltage across the cell is given by:

\[
E = \frac{RT}{4F} \ln \left( \frac{f_0^2(\text{unknown})}{f_0^2(\text{reference})} \right)
\]

(2.2)

where \( E \) is the voltage, \( R \) is the gas constant, \( T \) is the temperature in
Kelvin, and $F$ is the Faraday constant. With a pure oxygen reference gas the oxygen fugacity is given by:

$$\log f_{O_2} = \frac{20.159}{T} \left( \frac{E}{T} \right)$$

(2.3)

where $T$ is the temperature in Kelvin and $E$ is in millivolts.

The fugacity probe was calibrated against the iron-wustite (IW) buffer (equation 3.2). Pure Fe wires were held either just above or just below the IW buffer for one day. The oxidized wire is visibly darkened or recrystallized, crumbles when touched, and has a larger diameter than the original metal wire. The reduced wire remains ductile and retains its original diameter. Myers (1981) redetermined the equilibrium constant for the IW buffer, and placed the buffer approximately 0.2 log units more oxidizing at 1190°C than data from Robie, Hemingway and Fisher (1978). Our experience with the fugacity probe calibration procedure supported Myers' results. In addition, there is close agreement between the $f_{O_2}$ determined from the fugacity probe and the $f_{O_2}$ calculated using Myers' thermodynamic data from the mole fractions of Fe and FeO in metal and silicate respectively. For these reasons we believe that all of the experiments listed in Table 1 were run at an oxygen fugacity within $\pm 0.1$ log units of $-13.4$.

Temperature was monitored continuously during the experiments with a Pt100-Pt90Rh10 thermocouple. The thermocouple was calibrated against the melting point of gold wire (1063°C). Thermocouple accuracy was better than $\pm 30^\circ C$. Samples were placed in alumina crucibles.
**TABLE 1**

RESULTS OF METAL-SILICATE PARTITIONING EXPERIMENTS FOR W

<table>
<thead>
<tr>
<th>EXPERIMENT</th>
<th>DURATION IN DAYS</th>
<th>D(W)</th>
<th>W IN METAL WT% W</th>
<th>W IN SILICATE WT% W</th>
<th>STARTING W</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS5</td>
<td>10</td>
<td>25.3 ± 3.8</td>
<td>1.95 ± 0.09</td>
<td>0.077 ± 0.011</td>
<td>W metal</td>
</tr>
<tr>
<td>MS8</td>
<td>6</td>
<td>18.4 ± 2.0</td>
<td>4.29 ± 0.20</td>
<td>0.233 ± 0.024</td>
<td>WO3</td>
</tr>
<tr>
<td>MS9</td>
<td>12</td>
<td>29.3 ± 2.2</td>
<td>4.42 ± 0.05</td>
<td>0.151 ± 0.011</td>
<td>W metal</td>
</tr>
<tr>
<td>MS11</td>
<td>8</td>
<td>21.1 ± 1.4</td>
<td>4.16 ± 0.08</td>
<td>0.197 ± 0.012</td>
<td>WO3</td>
</tr>
<tr>
<td>MS11a</td>
<td>13</td>
<td>30.3 ± 2.8</td>
<td>4.33 ± 0.09</td>
<td>0.143 ± 0.013</td>
<td>both</td>
</tr>
<tr>
<td>MS7d</td>
<td>8</td>
<td>47.8 ± 7.2</td>
<td>3.25 ± 0.06</td>
<td>0.068 ± 0.010</td>
<td>W metal</td>
</tr>
<tr>
<td>MS9c</td>
<td>9</td>
<td>45.8 ± 7.5</td>
<td>3.30 ± 0.06</td>
<td>0.072 ± 0.012</td>
<td>W metal</td>
</tr>
</tbody>
</table>
suspended in the muffle tube. Samples were quenched by immersion in water. We attempted to evaluate the temperature inside the crucibles. An experiment was run using the broken electrical circuit method, in which gold wire was suspended within a crucible but above an experimental charge. This test indicated that temperatures inside the crucible may be no more than 70°C lower than the temperature of the hot spot recorded by the thermocouple outside of the crucible.

The experimental charges consisted of a mixture of pure Fe metal (325 mesh) and silicate of the following composition: 11 wt.% CaO, 13 wt.% Al₂O₃, 50 wt.% SiO₂, 7 wt.% MgO, 19 wt.% FeO. The silicate composition is approximately the same as the eucrite Juvinas (Stolper, 1977). Tungsten was added either as WO₃ powder or as W metal (100 mesh). Phosphorus was added either as P₂O₅ or as P (red P). The experimental mixtures were then shaken in a ball mill for 20 minutes. The ratio of metal to silicate is one-to-one by volume. During the run the metal-silicate mixture forms a pillar (~10 mm high, ~5 mm diameter) separated from the walls of the crucible.

Interior slices of the experimental products were analyzed using an ARL SEMQ electron microprobe. A pure W metal standard was used for W, and an apatite standard was used for P. A ZAF correction program was used for determining the W and P content of the metal and silicate phases. A typical counting time of 40 seconds on the WMα peak resulted in approximately 1.3% counting statistics for each metal analysis. A minimum of fifteen metal phase analyses were completed for each W partition coefficient determination. Typical counting times of 300 to
500 seconds (depending on W concentration) on the WM$_\alpha$ peak resulted in counting statistics of approximately 6% for each silicate analysis. In general a minimum of eight silicate phase analyses were completed for each D(W), (except for samples MS-7d and MS-9c where four analyses were obtained on each phase). A very small correction of 0.025 to 0.04 wt% was added to the concentration of W in the silicate phase because an interference near the WM$_\alpha$ peak resulted in an over-estimation of background intensity. This correction was determined by 10 to 20 peak counts of long duration (400-800 seconds) on W-free glass of the experimental composition. An addition of 0.02 wt.% to the concentration of W in the metal phase was found to be also necessary and was determined in a similar manner.

An average of ten analyses of both the metal and silicate phases were obtained for each P experiment (Table 2). For experiments P-4 to P-11, a small correction of +0.034 wt.% was added to each silicate analysis, because an interference near the PK$_\alpha$ peak resulted in an over-estimation of the background. A different background setting for P-12 to P-19 resulted in a required small correction of -0.006 wt.% P. The corrections were determined by 10-20 peak counts of long duration (300 seconds) on a P-free glass of the experimental composition.

2.2 EXPERIMENTAL RESULTS

The experimental run products are an intimate mixture of metal and silicate glass on a 100 micron size scale. Rare skeletal quench crystals were occasionally observed optically in the silicate glass, but
### Table 2

RESULTS OF METAL-SILICATE PARTITIONING EXPERIMENTS FOR W

<table>
<thead>
<tr>
<th>EXPERIMENT</th>
<th>DURATION IN DAYS</th>
<th>D(P)</th>
<th>P IN METAL</th>
<th>P IN SILICATE</th>
<th>STARTING P</th>
<th>TEMP. °C</th>
<th>LOGF O₂</th>
</tr>
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<tr>
<td>P-4</td>
<td>6</td>
<td>2.68 ± 0.33</td>
<td>1.61 ± 0.02</td>
<td>0.600 ± 0.07</td>
<td>P</td>
<td>1190</td>
<td>-13.52</td>
</tr>
<tr>
<td>P-5</td>
<td>6</td>
<td>1.14 ± 0.10</td>
<td>1.28 ± 0.03</td>
<td>1.12 ± 0.09</td>
<td>P₂O₅</td>
<td>1190</td>
<td>-13.23</td>
</tr>
<tr>
<td>P-6</td>
<td>12</td>
<td>0.676 ± 0.077</td>
<td>1.56 ± 0.15</td>
<td>2.31 ± 0.14</td>
<td>P₂O₅</td>
<td>1190</td>
<td>-12.98</td>
</tr>
<tr>
<td>P-7</td>
<td>12</td>
<td>1.09 ± 0.08</td>
<td>1.40 ± 0.08</td>
<td>1.28 ± 0.05</td>
<td>P</td>
<td>1190</td>
<td>-13.15</td>
</tr>
<tr>
<td>P-8</td>
<td>7</td>
<td>0.491 ± 0.011</td>
<td>0.973 ± 0.010</td>
<td>1.98 ± 0.04</td>
<td>P</td>
<td>1190</td>
<td>-12.93</td>
</tr>
<tr>
<td>P-9</td>
<td>7</td>
<td>1.09 ± 0.04</td>
<td>1.41 ± 0.02</td>
<td>1.29 ± 0.03</td>
<td>P₂O₅</td>
<td>1190</td>
<td>-13.13</td>
</tr>
<tr>
<td>P-10</td>
<td>6</td>
<td>1.60 ± 0.12</td>
<td>0.693 ± 0.011</td>
<td>0.435 ± 0.031</td>
<td>P</td>
<td>1190</td>
<td>-13.34</td>
</tr>
<tr>
<td>P-11</td>
<td>6</td>
<td>4.40 ± 0.46</td>
<td>0.797 ± 0.017</td>
<td>0.181 ± 0.019</td>
<td>P₂O₅</td>
<td>1190</td>
<td>-13.64</td>
</tr>
<tr>
<td>P-12</td>
<td>6</td>
<td>18.7 ± 1.8</td>
<td>0.806 ± 0.018</td>
<td>0.043 ± 0.004</td>
<td>P</td>
<td>1300</td>
<td>-12.49</td>
</tr>
<tr>
<td>P-13</td>
<td>6</td>
<td>17.7 ± 1.3</td>
<td>0.778 ± 0.024</td>
<td>0.044 ± 0.003</td>
<td>P₂O₅</td>
<td>1300</td>
<td>-12.47</td>
</tr>
<tr>
<td>P-14</td>
<td>8</td>
<td>5.60 ± 0.20</td>
<td>0.623 ± 0.014</td>
<td>0.111 ± 0.003</td>
<td>P</td>
<td>1300</td>
<td>-12.06</td>
</tr>
<tr>
<td>P-15</td>
<td>8</td>
<td>4.27 ± 0.33</td>
<td>0.683 ± 0.020</td>
<td>0.160 ± 0.011</td>
<td>P₂O₅</td>
<td>1300</td>
<td>-12.06</td>
</tr>
<tr>
<td>P-16</td>
<td>8</td>
<td>19.2 ± 1.0</td>
<td>0.748 ± 0.008</td>
<td>0.039 ± 0.002</td>
<td>P</td>
<td>1300</td>
<td>-12.48</td>
</tr>
<tr>
<td>P-17</td>
<td>8</td>
<td>23.9 ± 5.0</td>
<td>0.764 ± 0.005</td>
<td>0.032 ± 0.007</td>
<td>P₂O₅</td>
<td>1300</td>
<td>-12.47</td>
</tr>
<tr>
<td>P-18</td>
<td>7</td>
<td>2.22 ± 0.09</td>
<td>0.639 ± 0.010</td>
<td>0.288 ± 0.011</td>
<td>P</td>
<td>1300</td>
<td>-11.86</td>
</tr>
<tr>
<td>P-19</td>
<td>7</td>
<td>2.36 ± 0.07</td>
<td>0.689 ± 0.006</td>
<td>0.292 ± 0.008</td>
<td>P₂O₅</td>
<td>1300</td>
<td>-11.88</td>
</tr>
</tbody>
</table>
no chemical variations attributable to quench crystals were detected. The analyses listed in Tables 1 and 2 and plotted in Figures 1 and 2 were measured on adjoining metal and silicate areas. The run products for the W experiments are generally homogeneous within each phase, but very small local metal areas with higher W concentrations do exist in some samples and may represent the α-structural phase (Hansen, 1958). These isolated W-enriched areas are visible petrographically as areas consisting largely of metal with minor silicate. Most of the visible area of the W runs, however, have metal and silicate in a ratio of approximately 1 to 1. The run products for the P experiments are apparently homogeneous as no significant variations in P concentrations were detected within the metal or silicate phases.

Five W experiments (MS-5,-8,-9,-11,-11a) yielded a W partition coefficient of $25 \pm 5$ at approximately 1190°C and log $f_{O_2} = -13.4$ (Table 1), conditions approximating the eucritic liquidus (Stolper, 1975, 1977). Two types of experiments were run in an attempt to demonstrate equilibrium partitioning. The first type is illustrated by experiments MS-5, -8, -9 and -11. In experiments MS-5 and MS-9, W was present in the starting mixture in metallic form. In experiments MS-8 and MS-11, W was originally present in oxidized form as WO$_3$. As expected, experiments starting with W metal have slightly higher metal/silicate partition coefficients than experiments starting with WO$_3$. In the second type of experiment, experimental charges (MS-7d, MS-9c) were first run at a much lower oxygen fugacity than that appropriate to the eucritic liquidus, resulting in most of the W dissolving in the
INITIAL STATE of W:

- **W** - metal
- **WO_3**
- **W** - metal + **WO_3**
- Run first at low **f_0_2**
- Rerun at eucrite conditions

Figure 1. Solid-metal/silicate-melt partition coefficient **D(W)** versus wt% W in the silicate phase. -- Data from Table 1. Error bars are 1 σ.
Figure 2. Log $D(P)$ versus log $f_{O_2}$ from experimental data listed in Table 2. Data for two temperatures, 1190°C, and 1300°C are plotted. The initial state of $P$ in the experimental charge is indicated by squares for $P$ (red $P$) and circles for $P_2O_5$. 
metal phase and yielding $D(W) > 100$. The same charges were then rerun at the oxygen fugacity appropriate to eucritic liquidus conditions with the result that the partition coefficients (Fig. 1) approached values obtained in the first set of experiments but did not reach the equilibrium value of $D(W)$. The wide range of the individual analyses may be due to the failure of these experiments (MS-7d, MS-9C) to reach equilibrium. Additional support for an equilibrium value at $D(W) = 25$ comes from the small difference between experiments MS-ll and MS-lla. Experiment MS-ll was run for 8 days. A slice of the charge was then removed and analyzed, while the remainder of the charge (MS-lla) was run for an additional 13 days. The values of $D(W)$ for MS-ll and MS-lla are 21 and 30 respectively, indicating only a small change in $D(W)$. The variability among the different experiments in Table 1 may be due to a slight variability in the actual oxygen fugacity and temperature in each run, to which $D(W)$ is very sensitive in this range.

Because of the limited sensitivity of the electron microprobe the experiments were doped with W to very high concentrations compared to natural systems. Rammensee and Wänke (1977) using a neutron activation technique, however, found no deviations from Henry's Law behavior over a wide range in W concentrations. The experiments reported here showed no significant deviation in $D(W)$ over a factor of two in W concentration (Table 1), although the experiments were at higher W concentrations than Rammensee and Wänke's. Extrapolation of the results of Rammensee and Wänke to 1190°C gives a value of $D(W)=17$, in acceptable agreement with our results. A Henry's law effect is
unlikely to be a problem for the P experiments because, since P is a minor element, the concentrations of P used in the experiments are closer to those in natural systems.

For the P experiments, the experimental solid-metal/silicate-melt partition coefficients, \( D(P) \), form parallel trends at 1190\(^\circ\)C and 1300\(^\circ\)C. Linear regressions yield:

\[
1190\,\text{C}: \quad \log D(P) = -1.21 \log f_{02} - 15.95, \quad r^2 = 0.980 \quad (2.4)
\]

\[
1300\,\text{C}: \quad \log D(P) = -1.53 \log f_{02} - 17.73, \quad r^2 = 0.986 \quad (2.5)
\]

The slope for the 1190\(^\circ\)C data is probably more accurate, because of the large uncertainties for the four experiments with the highest \( D(P) \) at 1300\(^\circ\)C (see experiments P-12, P-13 and P-16, P-17 in Table 2).

The valence state of P may be determined from the slope of the data in Figure 2 by considering the thermodynamic derivation of the partition coefficient:

\[
P(\text{met}) + y \, O_2(\text{gas}) = P_{O_2y}(\text{sil}) \quad (2.6)
\]

The partition coefficient \( D(P) \) may be approximated as

\[
\log D(P) = -y \log f_{02} + \log \frac{\gamma P_{O_2y}(\text{sil})}{\gamma P(\text{met})} + "\text{constant}" \quad (2.7)
\]

where the "constant" contains \( \Delta \mu_0 /RT \) (the difference between standard state chemical potentials) and a factor accounting for the conversion from mole percent to weight percent. \( \gamma P_{O_2y}(\text{sil}) \) and \( \gamma P(\text{met}) \) are the activity coefficients for P in silicate and metal respectively. The
ratio of the two activity coefficients can be assumed to be constant in the Henry's law region of P concentrations. For the additional assumptions of a valence state of 5 for P in silicates, a slope (y) of -1.25 is calculated. The slopes obtained by a linear regression of the data (-1.21, -1.53) are close to this value, supporting a valence state of 5 for P in silicate liquid under the experimental conditions, providing that the assumptions of a constant difference in chemical potentials and a constant ratio of activity coefficients is correct.
CHAPTER 3

GEOCHEMICAL BEHAVIOR OF TUNGSTEN AND PHOSPHORUS

The behavior of W during nebular condensation is incompletely understood. At high temperatures W is associated with refractory noble metals which are embedded in refractory Ca-Al-rich silicate inclusions or oxide inclusions (Wänke et al., 1974; Palme and Wlotzka, 1976). At lower temperatures, W appears to have been present primarily as an oxidized species in the material which accreted to form the ordinary chondrites. This is indicated by the low concentration of W in metallic nickel-iron in unequilibrated ordinary chondrites and by the approximately constant W/La ratios in ordinary chondrites of widely varying metal content. This conclusion is also supported by the work of Rambaldi and Cendales (1977) who suggested, on the basis of the approximately constant W/Fe ratio in the ordinary chondrites, that W was substantially present in oxidized form during metal-silicate fractionation in the solar nebula.

Wänke et al. (1973) reported that the Earth, Moon and EPB have W/La ratios which correspond to depletions of W relative to La by factors of approximately 19 compared to chondrites. More recent data (Fig. 3) shows that primary eucritic magmas are slightly more depleted in W relative to La, by a factor of 31 ± 8 (Palme and Rammensee, 1981). In view of the evidence for the behavior of W primarily as an oxidized species in nebular condensates available for planetary body assembly,
Figure 3. Concentrations of W and La in eucrites. — The reference line labelled "Moon" is the average W/La ratio for lunar samples. The eucrite and lunar data are from Palme and Rammensee (1981) and references therein. The Cl, H, L and LL chondrite data (in Figs. 3, 4, 5, 7, 9, and 10) are a combination of data from Mason (1979), Palme, Suess, and Zeh (1981), and Rambaldi, Wänke, and Larimer (1979). The eucrite abbreviations for Figs. 3, 5 and 8 are as follows: JU = Juvinas, SC = Sioux County, PA = Pasamonte, IB = Ibitira, ST = Stannern, BO = Bouvante, BE = Bereba, YA = Yamato 74-450, SD = Serra de Mage, CA = Cachari, NL = Neuvo Laredo, MC = Moore County, HA = Haraiya, AH = Allan Hills 77005, BI = Binda, JO = Jonzac, MA = Macabini, PO = Pomozdino.
Figure 3. Concentrations of W and La in eucrites.
this reduction in the W/La ratio is generally attributed to metal-silicate partitioning of W subsequent to planetary formation.

$P/\text{La}$ ratios are also reduced in the Earth, Moon and EPB relative to chondrites (Figs. 4, 5). Wai and Wasson (1977) have calculated that $P$ condenses in solution with Fe-Ni metal from a gas of solar composition by the reaction:

$$\text{PN}(\text{gas}) = \text{Psolid} + \frac{1}{2} \text{N}_2(\text{gas}). \quad (3.1)$$

The 50% condensation temperature of $P$ at $10^{-4}$ atm falls between the condensation temperature of Fe and Au (Fe at 1336°C, $P$ at 1290°C, Au at 1230°C). The relatively high condensation temperature suggests that volatility of $P$ is unlikely to be responsible for the large depletion of $P$ relative to La observed in the Earth, Moon and EPB. The similarity of $P$ abundances in the Cl chondrites and the three classes of ordinary chondrites also suggests that nebular fractionation of $P$ was small, which supports the assumption that the abundance of $P$ in the Earth, Moon and EPB is close to chondritic.

The important factors controlling the partitioning of $W$ and $P$ between metal and silicate phases subsequent to planetary assembly are oxygen fugacity, temperature, pressure, degree of partial melting and the compositions of the solid and liquid metal and silicate. If the oxidation state is unknown, the oxygen fugacity may be calculated from estimates of the FeO content of the silicates and the Fe content of the coexisting metal. The calculation of oxygen fugacity from the
Figure 4. Concentrations of P and La in lunar and terrestrial samples.

-- The lunar data are from Palme et al. (1978) and references therein.

The terrestrial basanite and lherzolite data are from Basaltic Volcanism (1981).
Figure 5. Concentrations of P and La in eucrites. The source of data is an unpublished compilation of eucrite analyses (Mittlefehldt, 1980 personal communication). The lunar P/La trend is from Fig. 4.
activities of Fe and FeO in experiments or in planets is based on the calibration of the iron-wustite buffer by Myers (1981):

$$\log f_{O_2} = -26834.7/T + 6.471 \pm 0.058$$  \hspace{1cm} (3.2)

where T is temperature in Kelvin. For variable activities of Fe and FeO we have:

$$Fe + 1/2O_2 = FeO$$  \hspace{1cm} (3.3)

$$\Delta G^0 = -RT \ln \frac{a_{FeO}}{a_{Fe} \cdot f_{O_2}^{1/2}}$$  \hspace{1cm} (3.4)

$$\log f_{O_2} = \frac{-2 \Delta G^0}{2.303 RT} - 2 \log a_{FeO} + 2 \log a_{Fe}$$  \hspace{1cm} (3.5)

combining equations 3.2 and 3.5 the oxygen fugacity can be calculated from:

$$\log f_{O_2} = -26834.7/T + 6.471 - 2 \log a_{FeO} + 2 \log a_{Fe}$$  \hspace{1cm} (3.6)

assuming ideal behavior.

At low degrees of partial melting, the concentrations of W and P in the silicate melt and in the metal are very large, because W and P as incompatible elements are substantially excluded from solid silicates. The relative proportion of different silicate mineral phases does not have much effect on the W/La and P/La ratios in the silicate
melts because of the incompatible nature of W, P and La. P-rich phases are unlikely to form, even at low degrees of partial melting, because very large concentrations of P are required to saturate basaltic liquids (Watson, 1980).

The partial melting calculations discussed in later chapters utilize an equilibrium partitioning model based on the formulation of Shaw (1970). The concentration of a trace element in a liquid produced by equilibrium partial melting of a polymineralic source region is given by the equation:

\[ C_l/C_o = 1/(F + D(1 - F)) \]  \hspace{1cm} (3.7)

where \( C_l \) is the concentration of the element in the liquid, \( C_o \) is the initial concentration in the bulk solid, \( F \) is the fraction of liquid, and \( D \) is the mean partition coefficient defined as \( D = \sum X_i D_i \) where \( X_i \) is the mass fraction of mineral \( i \) and \( D_i \) is the mineral/liquid partition coefficient for mineral \( i \).

The composition of the metal controls the partitioning behavior of P and W in two ways. First, composition determines the ratio of solid to liquid metal at a given temperature. Narayan and Goldstein (1982) and Jones and Drake (1982) have shown that P is preferentially partitioned into liquid metal (\( D = 0.1 \)). Second, the partitioning of P between solid and liquid metal depends upon the S concentration. Preliminary experiments of Jones and Drake (1982) have shown that the presence of S in metallic liquids reduces the metallic-liquid/silicate-melt partition coefficient for P and for W compared to S-free metallic
liquid at the same temperature. The minimum S content required for producing a metallic liquid is controlled by temperature, leading to fundamentally different partitioning behavior at different temperatures. An example is given in Table 3. For lunar temperatures (high) the minimum S-concentration in the metallic liquid is low (< 10% S), and therefore P partitions very strongly into the metallic liquid and W partitions equally well into either solid or liquid metal. For EPB temperatures (low) the minimum S-content of the metallic liquids is much higher (> 20% S), and therefore P is not as strongly partitioned into the metallic liquid and the affinity of W for the metallic liquid becomes almost negligible.

The effect of pressure on the partitioning behavior of W and P is unknown, but is probably less important than the effect of temperature and oxygen fugacity. As illustrated in Fig. 2 for P, only a small change in temperature or oxygen fugacity can change the geochemical behavior of W and P from siderophile to lithophile. In the EPB pressures were probably very low, less than one kilobar (Walker, Stolper and Hays, 1978). Most of the lunar mantle has also remained at relatively low pressures, with 54% of the Moon at pressures less than 20 kilobars. For the Earth, metal-silicate equilibrium may have been established at relatively low pressures in the upper mantle of the growing proto-Earth (see chapter 6).
Table 3

EXAMPLES OF P AND W PARTITION COEFFICIENTS

<table>
<thead>
<tr>
<th></th>
<th>EPB CONDITIONS</th>
<th>Lunar Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>W</td>
</tr>
<tr>
<td>Solid-metal/silicate-melt</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>solid-metal/metallic-liquid</td>
<td>0.3</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>metallic-liquid/silicate-melt</td>
<td>7</td>
<td>&lt;2.5</td>
</tr>
</tbody>
</table>

EPB conditions ≈ 1190°C, log fO₂ = -13.4

Lunar conditions ≈ 1300°C, log fO₂ = -12.6 for 13% FeO

Sources: Narayan and Goldstein (1982), Jones and Drake (1982)
CHAPTER 4

EUCRITE PARENT BODY

Petrogenetic processes that account for the depletion of P and W relative to La in the eucrites fall into three main categories. First, there are processes involving equilibrium between metal and silicates during high degrees of partial melting or total melting of the EPB mantle, followed by fractional crystallization to produce the eucrites. Second, there are processes involving equilibration and separation of metal and silicates in the EPB mantle prior to the melting of the silicates to produce eucrites. Third, there are processes involving equilibration and separation of metal and silicates during low degrees of partial melting of the EPB mantle, with additional melting producing the eucrites. Within each category the possibility of a heterogeneous or homogeneous distribution of metal must be considered. The petrogenetic model that is most reasonable must be compatible with the siderophile element data, in addition to being physically plausible. These models are discussed below and are summarized in Table 4.

4.1 Equilibrium between metal and silicate during extensive melting

This model assumes equilibrium is maintained between metal and silicates at high degrees of partial melting or total melting of the EPB. Because metal would settle gravitationally to form a metal core before total melting is accomplished, equilibrium must be maintained
Table 4
MODELS FOR METAL-SILICATE SEPARATION IN THE EUCRITE PARENT BODY WITH SOLID-METAL CONTENTS BASED ON PARTITIONING OF W

<table>
<thead>
<tr>
<th>METAL-SILICATE EQUILIB. MODEL</th>
<th>MAGMA FORMATION</th>
<th>METAL DISTRIBUTION</th>
<th>CONSISTENT WITH Co</th>
<th>METAL CONTENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Total melting</td>
<td>fract. cryst.</td>
<td>homogen.</td>
<td>yes</td>
<td>25-38%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>or heterogen.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Subsolidus separation</td>
<td>partial melt</td>
<td>heterogen.</td>
<td>no</td>
<td>10-50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>homogen</td>
<td>yes</td>
<td>24%</td>
</tr>
<tr>
<td>3. Partial melt low F</td>
<td>partial melt</td>
<td>heterogen.</td>
<td>no</td>
<td>3-25%a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>homogen</td>
<td>yes</td>
<td>2-10%</td>
</tr>
</tbody>
</table>

aThis model requires the full range of metal contents from 3% to 25%.
between the core and the liquid silicate despite the large distance for diffusion and the possibility that a layer of dense residual crystalline silicate (e.g., olivine) could isolate the core. Rapid convection may therefore be required in both the silicate melt and in the metal core. A potent heat source is also required for this model. Several sources, for example, Al26 and electromagnetic heating (Sonett and Reynolds, 1979) have been proposed, but it is problematical that they were extant during the required time interval.

The bulk solid metal content required to lower the W/La ratio during extensive melting may be calculated by the formula: 

\[ x = \frac{(a-1)}{(D+a-1)} \]

where \( D \) is the metal/silicate partition coefficient and \( a \) is the depletion factor for the W/La ratio (Rammensee and Wänke, 1977). Palme and Rammensee (1981) obtained a metal content of \( 37 \pm 5\% \) for the EPB by assuming a depletion factor of \( 31 \pm 8 \) and \( D(W) = 53 \). The value of \( D(W) = 53 \) used by Palme and Rammensee (1981) is for a temperature of \( 13000^\circ C \) (appropriate to total melting) and for \( \log fO_2 = -12.55 \). In the idealized case, metal forms a core before equilibrium ceases, and there is no practical distinction between the final result for total melting, regardless of whether metal was initially homogeneously or heterogeneously distributed.

At lower but still substantial degrees of partial melting the amount of solid metal required is less because of the incompatible nature of W. Tungsten is excluded from solid silicates so that during partial melting almost all of the W is forced into the solid or liquid metal and liquid silicate phases.
The concentration of W in the metal is much higher at lower degrees of partial melting than if the silicates are totally molten. The lower limit of partial melting for this mechanism is the highest degree of partial melting represented by the eucrites, approximately 15%. As demonstrated below, the equilibrium metal content required at \( P = 0.15 \) is approximately 25% metal. The range of metal contents required by this process (25%-37%) is outside the range of metal content in the ordinary chondrites (0.3-19%; Wasson, 1974), meteorites which may be considered as representative of the nonvolatile material available for planetary assembly.

A major problem with extreme melting of the EPB is the requirement that the eucrite magmas were formed by fractional crystallization from a single magma. Early models did explain the eucrites as residual liquids from fractional crystallization of an unsampled primary magma (Mason, 1962, 1967; Bunch, 1975). Stolper (1977), however, showed that the major and trace element compositions of the eucrites were inconsistent with formation from a single primary magma by fractional crystallization. Stolper (1977) and Consolmagno and Drake (1977) demonstrated that the main group and the Stannern trend of eucritic magmas could be produced by equilibrium partial melting of a single primitive source region. The Nuevo Laredo trend appears to require fractional crystallization, possibly of a main group magma. Equilibrium crystallization could produce magmas identical to those produced by equilibrium partial melting, but this mechanism is
physically improbable (Stolper, 1977). More complicated multiple stage melting or crystallization schemes can probably be excluded based on the ancient crystallization ages of the eucrites, at $4.54 \pm 0.02$ b.y. (Basaltic Volcanism, 1981).

Because total melting of the EPB in the absence of a demonstrably adequate heat source is implausible, coupled with a physically improbable mechanism for generating eucritic magmas, extensive melting of the EPB is an unlikely possibility.

4.2 Subsolidus separation of metal

In this model, metal separates from the silicate before the silicates melt. The separation of metal is governed by the abundance and size-frequency distribution of the metal, the amount of time available, EPB gravity, and the viscosity of the EPB mantle. Perhaps the most critical parameter is viscosity. Viscosity varies tremendously from a solid unmelted mantle to a completely molten magma ocean. The high viscosity of an unmelted EPB mantle could possibly be offset by formation of a sulfur-bearing metallic liquid at temperatures above 1000°C, but it is uncertain if the S abundance of the EPB is adequate (Newsom and Drake, 1979; Basaltic Volcanism, 1981).

The metal-silicate partitioning data from ordinary chondrites provide a means for understanding the partitioning behavior of W at subsolidus temperatures (Rambaldi and Cendales, 1977). Because all three classes of ordinary chondrites have members with partition coefficients greater than 100 (type 6), we adopt 100 as a reasonable
value for the metal/silicate partition coefficient during the subsolidus separation, especially since the measured partition coefficients may be affected by contamination of the silicates by metal. The metal/silicate partition coefficient values deduced from chondrites are applicable to the EPB since the eucrite source region is essentially chondritic in a temperature-oxygen fugacity plot (Fig. 6). For subsolidus separation of solid metal to account for the reduced W/La ratios, 24% metal is required, assuming a partition coefficient of 100 and a depletion factor of 31.

The metal distribution must be relatively homogeneous to produce the relatively constant W/La ratios observed in the eucrites. A heterogeneous metal content requires an unlikely covariance of partition coefficient with metal content. For a range of partition coefficients from 35 to 230, the metal contents could range from 10% to 50%.

A major difficulty with subsolidus separation of metal is that of achieving complete metal separation from the silicates. Some metal segregation may begin at subsolidus temperatures, but complete separation of metal from silicates is unlikely prior to partial melting of silicates and concomitant reduction of mantle viscosity. This process is therefore also considered to be unlikely.

4.3 Metal separation at low degrees of partial melting

For equilibration and separation of metal from silicate at low degrees of partial melting we can apply the experimentally determined D(W) because the actual behavior of W during partial melting in the
Figure 6. Subsolidus $T$-$fO_2$ paths for the EPB and the ordinary chondrites. -- The $T$-$fO_2$ paths are calculated using the method of Williams (1971), assuming a pressure of 3 kb. For the reaction:

$$Fe + \frac{1}{2} O_2 + FeSiO_3 = 2FeSi_{1/2}$$

Williams (1971) determined that:

$$\log K = \frac{13,778}{T} - 3.07 - \frac{23.9P}{T}$$

where $T$ is temperature in Kelvin and $P$ is pressure in kilobars. The compositions of the ordinary chondrites are from Van Schmus (1969). The $T$-$fO_2$ path for the EPB was constrained to pass through the solidus point for the EPB ($T = 1180^\circ C, \log fO_2 = -13.4$, Stolper, 1975). The $T$-$fO_2$ curves for the ordinary chondrites in Fig. 2 of Williams (1971) are incorrect due to an arithmetic error (personal communication, Williams, 1979).
Figure 6. Subsolidus T-fO$_2$ paths for the EPB and the ordinary chondrites.
presence of metal can be calculated. The W and La concentrations in a silicate melt have been calculated and are plotted in Fig. 7 for a range in the degree of partial melting, and with the assumption of different amounts of metal in the source region. Because no experimental solid/liquid silicate partition coefficients for W are known, the partition coefficient of W is assumed to be identical to that for La. D(W) is also assumed to be independent of melt composition, noting that the experimental eucrite composition should be appropriate to the calculations.

Heterogeneous metal distribution:

The results of the calculations plotted in Fig. 7 allow us to examine two possibilities for metal separation at low degrees of partial melting. The first possibility is the situation where metal is present in the source regions during the partial melting event that produced the eucrites. As illustrated by Fig. 7, this possibility requires that the source regions contained variable metal contents (3% to 25%) because the presence of metal in the source regions buffers the W content of the melt.

The substantial heterogeneity in the distribution of metal within the EPB deduced from this model is in contrast to the relative homogeneity of metal distribution in each class of ordinary chondrites. In addition, covariance between the metal content and the degree of partial melting is required in order to produced the relatively constant
Figure 7. The effect of source region solid-metal content on the W and La concentrations in eucritic silicate liquids. The lines labeled with different metal contents illustrate the dependence of the W and La concentrations in eucritic liquids on the metal content of the source region and on the degree of partial melting ($F$). The calculation utilized an equilibrium partial melting model (equation 3.7) assuming initial W and La starting concentrations of 150 ppb W and 3.3 ppm La. The assumed source region compositions are based on the work of Consolmagno and Drake (1977). The source region compositions are as follows: metal $x\%$, olivine $85\% - x\%$, plagioclase $5\%$, clinopyroxene $5\%$, orthopyroxene $5\%$. The nonmodal melting proportions are 40% plagioclase, 30% clinopyroxene, 30% orthopyroxene. Mineral-melt partition coefficients for W are assumed to be the same as for La and are: olivine, 0.01; low-calcium pyroxene, 0.006; high-calcium pyroxene, 0.07; plagioclase, 0.14. (Consolmagno and Drake, 1977). The degree of partial melting $F$ is the fraction of silicate liquid divided by the fractions of metal + solid silicate + melt. Dots are eucrite compositions from Fig. 5.
Figure 7. The effect of source region solid-metal content on the W and La concentrations in eucritic silicate liquids.
W/La ratios observed in the eucrites. These observations raise problems which do not arise with the alternative below.

Homogeneous metal distribution:

The alternative is that the metal was homogeneously distributed and separated from the eucrite source regions at very low degrees of partial melting before the eucritic magmas were generated. The degree of partial melting represented by the eucritic magmas is between 4% and 15% based on modeling of rare earth element abundances, assuming an initially chondritic abundance of REE (Consolmagno and Drake, 1977). Metal separation before partial melting reached 4% could have reduced the W/La ratio in the silicate source region to the present eucrite value. Subsequent partial melting or crystallization in the absence of metal would not significantly alter the W/La ratio because both elements are almost identically incompatible in the absence of metal. If, for example, the metal separated out just as the degree of partial melting represented by Stannern and Bouvante was reached, then as Fig. 7 indicates, a metal content of 3% in the source region is required to achieve the necessary W/La ratios. Note that the 3% metal line in Fig. 7 represents the liquid composition. The corresponding W and La concentrations in the solid silicates yield the same W/La ratio, at much lower absolute abundances.

Fig. 7 clearly indicates that at low degrees of partial melting the eucritic W/La ratio is reached with small metal contents. At low metal contents, however, another problem becomes important. Anders
(1964) showed that a definite relationship exists between the amount of metal in ordinary chondrites and the concentration of nickel in the metal. Chondrites with 3% metal have approximately 30% Ni in the metal. In order to remain in the range of \( f_{O_2} \) for the eucrites as determined by Stolper (1977) the FeO content must decrease if the Ni content increases. The possible range in oxygen fugacity for the eucrites (\( \log f_{O_2} = -13.3 \pm 0.2 \)), determined by Stolper (1977), leaves room, however, for most of the proposed estimates of the FeO content for the eucrites, which vary from 11% (Vizgirda and Anders, 1976) to 28% (Consolmagno and Drake, 1977).

Only broad limits can actually be placed on the metal content if it were homogeneously distributed because of experimental uncertainties in determining \( D(W) \) and the uncertain \( f_{O_2} \) during eucrite formation. Nevertheless, a relatively small metal content, perhaps a maximum of 10%, is predicted. This metal contains relatively high Ni contents (> 10% Ni). Metal contents of less than 2% are not likely because the Ni content in the metal (> 50% Ni) would probably result in an oxygen fugacity greater than the range suggested by Stolper (1977).

An additional consideration concerns the need to generate an approximately constant \( W/\text{La} \) ratio in the eucrite source region. The \( W/\text{La} \) ratio varies relatively rapidly with the degree of partial melting and with the actual metal content (Fig. 7). Several processes may lead to a relatively constant \( W/\text{La} \) ratio. The actual separation of metal can occur over a range of the degree of partial melting. This
separation of metal from silicate depends on the size-frequency distribution of the metal. Also the size of the source region may have been sufficiently large that the effects of even large variations in metal content are masked by mixing of magma. The conclusion is that equilibration and separation of homogeneously distributed metal at low degrees of partial melting is the mechanism most consistent with eucritic W/La ratios. A solid metal content for the EPB between 2% and 10% is inferred.

4.4 Additional constraints

Cobalt

The data for siderophile elements such as Co and P provide additional tests of the models for metal-silicate fractionation discussed above. Cobalt may be used to address the problem of a partial melting versus fractional crystallization origin for the primary eucritic magmas. Because Co is a compatible element in olivine, pyroxene, and Fe-metal, the weighted mean of the individual solid/melt partition coefficients ($D$) is always greater than unity. Fractional crystallization of olivine and pyroxene should, therefore, produce a negative correlation of Co with La, while during partial melting the Co concentration is buffered by the solid phases. Low degrees of partial melting produce a relatively constant Co concentration in the melt, in either the presence or absence of Fe-metal (Fig. 8).

These theoretical predictions may be compared with the Co and La data of Palme and Rammensee (1981). Because the Co analyses are
Figure 8. Concentrations of Co and La in eucrites. -- The source of the data is Palme and Rammensee (1981). The horizontal line represents the dependence of the Co and La concentrations on the degree of partial melting for two separate cases: (a) no metal present in the source region and an initial Co concentration of 12 ppm or (b) 10% metal in the source region and an initial Co concentration of 410 ppm (0.41% Co in the metal). In both cases the Co concentration is essentially independent of the degree of partial melting. The calculation assumed an equilibrium partial melting model (equation 3.7). Solid/melt partition coefficients for Co are: olivine, 3.3; plagioclase, 0.049; low-Ca pyroxene, 2.0; high-Ca pyroxene, 1.2; metal, 1,000 (Irving, 1978; Hewins and Goldstein, 1974).
sensitive to metal contamination (Wänke, personal communication, 1981), the highest points (for Ibitira and Sioux Co.) will be ignored. Only one of the Sioux Co. points has a high Co concentration, and Ibitira is generally known to be an anomalous eucrite (Stolper, 1977). The remaining data show a slight decrease in Co content from the main group eucrites to Stannern, with Bouvante being much lower in Co than Stannern. The data suggest that Stannern and the main group eucrites could be related by partial melting, as required by the mechanism for metal separation at low degrees of partial melting. The high iron content of Bouvante, as well as the Co data, suggest that Bouvante is a member of the Nuevo Laredo trend eucrites, a subgroup of eucrites which have probably experienced some fractional crystallization (Christophe Michel-Levy et al., 1980; Basaltic Volcanism, 1981).

Besides being inconsistent with mechanisms requiring fractional crystallization, the Co data are also inconsistent with the mechanism that requires a heterogeneous metal distribution in the source regions during the partial melting event that produced the eucrites (Palme and Rammensee, 1981). For this mechanism the Stannern source region is predicted to have less metal than Juvinas (Fig. 7). The correspondingly higher Co concentrations in the metal, assuming a constant chondritic Co abundance, would produce an enrichment of Co in Stannern compared to Juvinas, in contrast to observation.
The actual Co/Fe ratio in the EPB metal should be approximately chondritic (Stolper, 1977). But the exact value is not well constrained due to the uncertainty in the metal/silicate partition coefficient for Co.

Phosphorus

The P/La ratio in the eucrites (Fig. 5) is depleted by a factor of approximately 40 relative to Cl chondrites (Dreibus, Spettel and Wänke, 1976). For conditions appropriate to eucrite petrogenesis ($T = 1190^\circ C$, $\log f_{O_2} = -13.4$, Stolper, 1975, 1977), any metallic liquid would be S-rich. An S-bearing metallic liquid is not required by the W data because in contrast to P, the preliminary experiments of Jones and Drake (1982) indicate that W is partitioned much more strongly into solid metal than into S-bearing metallic liquid.

An analysis of P/La ratios in eucrites provides additional constraints on the metal content and the process of metal-silicate fractionation in the EPB. For conditions appropriate to eucrite petrogenesis the experimental results (Fig. 2) indicate that the solid-metal/silicate-melt partition coefficient for P is approximately two. This low value indicates that partitioning of P into solid metal could not be responsible for lowering of P/La ratios in the eucrites relative to Cl chondrites ($40 \pm 15$, Table 5). The depletion may, however, be explained by partitioning of P into a S-bearing metallic liquid.
Table 5

P/La AND W/La RATIOS
AND DEPLETION FACTORS

<table>
<thead>
<tr>
<th></th>
<th>P/La</th>
<th>W/La</th>
<th>P/La Depletion Factor</th>
<th>W/La Depletion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>~4,120</td>
<td>= 0.363</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Moon</td>
<td>36 ± 8</td>
<td>0.019 ± 0.007</td>
<td>115 ± 25</td>
<td>19 ± 7</td>
</tr>
<tr>
<td>EPB</td>
<td>~100</td>
<td>= 0.012</td>
<td>40 ± 15</td>
<td>31 ± 8</td>
</tr>
<tr>
<td>Earth</td>
<td>~100</td>
<td>= 0.019</td>
<td>40 ± 15</td>
<td>~19</td>
</tr>
</tbody>
</table>

Data are from Palme and Rammensee (1981), Palme et al. (1981), Rammensee and Wänke (1977), and Figs. 3, 4 and 5.
At temperatures appropriate to eucrite petrogenesis, an S content of 20 to 25 wt% in a coexisting metallic liquid may be reasonable, considering the effect of Ni on the Fe-FeS phase diagram (Schürmann and Neubert, 1980). Preliminary experiments by Jones and Drake (1982) indicate that the solid-metal/metalllic-liquid partition coefficient for P may be approximately 0.3 at these S concentrations. The resulting metallic-liquid/silicate-melt partition coefficient is approximately seven. Assuming this partition coefficient and initially chondritic P and La concentrations, the calculations plotted in Fig. 9 demonstrate the relationship between the degree of partial melting of the silicates and the amount of metallic liquid required to achieve the observed depletion of P/La ratios in the eucrites compared to the Cl chondrite ratio. For example, at a degree of partial melting $F = 0.02$ a metallic liquid content of approximately 12% is required to achieve a depletion factor of 40. The calculations shown in Fig. 9 suggest that a metallic liquid content of 5 to 25% is a reasonable estimate for reducing the P/La ratios in the eucrite source regions. The metallic liquid content is poorly constrained due to large uncertainties in the partition coefficients, the initial P and La concentrations in the source regions, the P/La ratio in the eucrites, and the degree of partial melting during metal-silicate equilibration and separation. It is also unclear that the volatile-poor EPB contains an adequate amount of S to generate as much as 25% of an S-bearing metallic liquid (Basaltic Volcanism, 1981).
Figure 9. The effect of the source region content of S-bearing metallic liquid on the P and La concentrations in eucritic silicate liquids. The lines labeled with different metallic liquid contents illustrate how P and La concentrations in eucritic silicate liquids depend on the S-bearing metallic liquid content of the source region and the degree of partial melting (F). The calculation utilized an equilibrium partial melting model (equation 3.7). A metallic-liquid/silicate-melt partition coefficient of 7 was assumed for P. The silicate-mineral/silicate-melt partition coefficient used for P is 0.01 (Watson, 1980). The source region composition is listed in Fig. 7. The initial concentration of P is 1360 ppm, and of La is 0.33 ppm. The degree of partial melting (F) is the amount of silicate liquid divided by the amount of all the phases present. The unlabeled dots represent the eucrites plotted in Fig. 5.
Figure 9. The effect of the source region content of S-bearing metallic liquid on the P and La concentrations in eucritic silicate liquids.
The partitioning behavior of \( P \) provides an additional test of the total melting model for the formation of the EPB suggested by Palme and Rammensee (1981). These authors assume total melting of the silicates in the EPB at conditions of 1300°C and \( \log f_{O_2} = -12.55 \). At 1300°C the metal in the EPB is probably completely liquid. At this temperature a solid-metal/metalllic-liquid partition coefficient of 150, the calculated metal content is approximately 20% \( \pm \) 5%. This estimate is not consistent with the authors' estimate of metal content from the \( W/\text{La} \) ratios of 37% \( \pm \) 5% (Palme and Rammensee, 1981). The results of the \( P \) and \( W \) data together are not consistent with metal-silicate equilibrium in the EPB during total melting of the EPB.

Based on the metal-silicate partitioning behavior of \( P \) and \( W \), a consistent model may be constructed to explain the depletion of both the \( P/\text{La} \) and \( W/\text{La} \) ratios in the EPB. From the behavior of \( W \), the low \( W/\text{La} \) ratios in the eucrites can be explained by equilibration and separation of 2% to 10% solid metal at low degrees of partial melting \( (F = 0.01 \text{ to } 0.05) \) of the silicates prior to production of eucritic magmas. An additional 5% to 25% S-bearing metallic liquid is necessary to explain the \( P/\text{La} \) ratio for the same range in the degree of partial melting. Thus, the permissible range of metal content of the EPB is 7% to 35%. It is unlikely that the actual metal content, both liquid and solid, exceeds the maximum range observed in the ordinary chondrites (19%; Wasson, 1974). As an example, for 19% total metal at \( F = 0.03 \),
the eucrite source regions must equilibrate with 3% solid metal (Fig. 7) and 16% S-bearing metallic liquid (Fig. 9). This metal became isolated from the source region prior to generation of eucritic magmas.

4.5 **Comparison with an independent estimate of the EPB metal content**

We have calculated a solid-metal content of 2% to 10% and a metallic liquid content of 5% to 25% for the EPB assuming equilibrium of P, W and La among metal, solid silicates and liquid silicates at low degrees of partial melting. This metal content may be compared with an independent estimate. Morgan et al. (1978) estimated the metal content of the EPB to be 13% by an independent method which assumed that the refractory siderophile element Ir was introduced solely in a high temperature condensate. By estimating the amount of Ir in this condensate and the amount of the condensate in the EPB, Morgan et al. (1978) calculated the total amount of Ir in the source region, assuming that the Ir concentration of the EPB metal was the same as that in the IIE iron meteorites. Given uncertainties in assumptions in this work and the work of Morgan et al. (1978), the agreement is satisfactory.
CHAPTER 5

THE MOON

The Moon, Earth and eucrite meteorites display W/La ratios which are lower than those in chondrites (Wänke et al., 1973). This depletion can be attributed to metal/silicate fractionation. For the Moon, Rammensee and Wänke (1977) concluded that any geophysically reasonable metallic lunar core would be too small to explain the low W/La ratios in the Moon. It was therefore suggested that the Moon was depleted of W in a non-lunar igneous event, supporting the hypothesis that the Moon formed by fission from the proto-Earth, the upper portion of which was depleted in W due to terrestrial core formation (Rammensee and Wänke, 1977; Ringwood, 1979). This conclusion is implicitly based on a special case, namely equilibrium between metal and silicate phases with total melting of silicates. In the geologically more plausible case where metal fractionates from silicate at relatively low degrees of partial melting, the incompatible nature of W may negate this conclusion. A geophysically plausible metallic core can account for the depletion of W in lunar surface and, presumably, lunar mantle rocks. The low W/La ratio in the Moon cannot be used as unconditional evidence for a terrestrial origin of the Moon.
5.1 Metal-silicate fractionation in the Moon

The first question is the initial concentrations of W and La in the Moon or in precursor lunar material. The presence of correlated pairs of refractory lithophile elements (for example, Ba/La) with Cl ratios in the Earth, Moon and eucrites argues strongly for a chondritic W/La ratio in the Moon or precursor lunar material (Dreibus, Spettel, and Wänke, 1977). The abundances of W and La in lunar rocks and chondritic meteorites are plotted in Fig. 10. The magnitude of the lunar W/La depletion relative to Cl and ordinary chondrites was calculated from the data in Fig. 10 and is listed in Table 6. The range of depletion factors for the Moon relative to the chondrites is 19 to 29, but there are large uncertainties in these figures due to the uncertainties in both the lunar and chondrite W/La ratios.

The amount of metal that may be present in the Moon is considered next. Geophysical evidence for the metal content of the Moon is inconclusive. The tightest constraint on the size of a lunar core, by Hood et al. (1981) is a maximum radius \( \leq 360 \) km, corresponding to 2% metal. Other investigations find indirect indications of a metal core with a radius of 200 to 500 km (Russell, Coleman, Jr., and Goldstein, 1981; Stevenson and Yoder, 1981). A 500 km radius core corresponds to approximately 5.5% metal.

The S content of the lunar core is an important parameter. Brett (1973) proposed that the lunar core consisted of FeS. Ringwood (1979), however, presents several arguments against an S-rich lunar metal core. He points out that primitive lunar basalts are not
Figure 10. Concentrations of W and La in lunar rocks. -- References in Figs. 3 and 4.
<table>
<thead>
<tr>
<th>Chondrite type</th>
<th>W/La ratios</th>
<th>Depletion factors(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Moon/chondrite</td>
</tr>
<tr>
<td>Cl</td>
<td>0.36±0.04</td>
<td>19±7</td>
</tr>
<tr>
<td>H</td>
<td>0.55±0.06</td>
<td>29±11</td>
</tr>
<tr>
<td>L</td>
<td>0.45±0.11</td>
<td>24±10</td>
</tr>
<tr>
<td>LL</td>
<td>0.40±0.09</td>
<td>21±9</td>
</tr>
</tbody>
</table>

Lunar W/La ratio = 0.019 ± 0.007, references in Fig.3.
saturated with FeS and that the large depletions of other volatile elements indicates that the Moon probably did not accrete a significant amount of S. Ringwood (1979) also points out that since P and W are not chalcophile their depletion in the Moon could not be explained by partitioning into an FeS core. For these reasons the calculations described here will assume a low (<10%) S-content for the lunar metal core.

Tungsten

With information on the possible magnitudes of the lunar W/La depletion and the possible lunar metal content, the parameters which control the partitioning of W between metal and silicate in the Moon can be evaluated. The most important parameters are the degree of partial melting, because of the incompatible nature of W, and the metal/silicate-liquid partition coefficient for W. The partition coefficient depends on the oxidation state, which depends on the FeO content, the Ni content of the metal, and the temperature of the Moon. The bulk composition and, hence, oxidation state of the Moon, is uncertain. The effects of these parameters on the W/La ratio are illustrated in Figs. 11 and 12 and are discussed below.

The behavior of W at low degrees of partial melting is particularly important. Tungsten is an incompatible element, with siderophile affinities under lunar conditions of low oxygen fugacity. Therefore, W prefers metal to silicate melt and prefers silicate melt to silicate solid. At low degrees of partial melting the concentration of W in the
Figure 11. Constraints on the partitioning of W in the Moon. -- The sloping lines represent the combination of D(W) and degree of partial melting (F) required to achieve a given depletion factor (a) for the W/La ratio in the silicate melt, relative to the initial W/La ratio in the source region. The depletion factors for the lines plotted in the figure were chosen to illustrate the uncertainty in the actual W/La depletion factor for the Moon relative to the Cl and ordinary chondrites (Table 6).

Construction of the figure is discussed in section 5.1. The solid-silicate/liquid-silicate partition coefficients used for both W and La are listed in Fig. 7. The model lunar silicate composition used was Hodges and Kushiro (HK) in Warren and Wasson (1979). The two FeO scales plotted at the side of Fig. 2 were calculated by determining the log fO₂ for a given FeO content assuming 1300°C, ideal solution behavior, and 6% Ni or 52% Ni in the metal (Myers, 1981). The corresponding D(W) was then calculated from the relation log D(W) = \(-\log fO₂ -10.83\) determined experimentally by Rammensee and Wänke (1977).
Figure 11. Constraints on the partitioning of W in the Moon.
Figures 12a,b. Combination of percent partial melting and FeO content at 1300°C required to achieve a reasonable P/La depletion factor for the Moon. -- Lunar W/La depletion factors are listed in Table 6. Fig. 12a is for 2% metal containing 6% Ni, Fig. 12b is for 2% metal containing 52% Ni. The plots were derived graphically from Fig. 11.
silicate melt and in the metal is very high because W is substantially excluded from solid silicates. Partitioning of W between solid metal and liquid metal is unimportant because the partition coefficient is close to unity (Jones and Drake, 1982).

Fig. 11 illustrates that, at low degrees of partial melting, significant depletion of W relative to La can occur even if the solid-metal/silicate-melt partition coefficient D(W) is relatively small. The figure was constructed by calculating a metal/(silicate-melt + solid-silicate) partition coefficient (D) using an equilibrium partial melting model (equation 3.7) to obtain the concentration of W in the silicate melt (W$_1$). Assuming mass balance, D can then be calculated from:

$$D = \frac{D(W) \cdot W_1 \cdot (1-x_{\text{metal}})}{W_0 - (D(W) \cdot W_1 \cdot x_{\text{metal}})}$$  \hspace{1cm} (5.1)

where $W_0$ is the initial concentration of W in the source region. The diagonal lines represent the constant D necessary to achieve a given W/La depletion factor (a), assuming a metal content (x) of 2%. The relationship between D and the depletion factor was calculated from the equation $x = (a-1)/(D+a-1)$ (Rammensee and Wänke, 1977). Breaks in slope occur when phases are exhausted, but the changes are small and are not shown. The lines in the Fig. 11 can also be calculated more directly from the equilibrium partitioning model by finding the combination of D(W) and F required to achieve a given W/La depletion factor.

The degree of partial melting in the Moon during metal/silicate fractionation is important to determine because of its
large effect on the partitioning of W. In their calculations Rammensee and Wänke (1977) implicitly assumed that total melting of the silicates occurred, such that under these conditions a very large D(W) is required if a geophysically plausible metallic core is responsible for the depletion of W in the Moon. It seems more geologically plausible, however, that equilibrium between silicate and metal be confined to small degrees of partial melting, because metal will rapidly sink and the melt will rapidly rise before a large degree of partial melting can occur. As the metal starts sinking and aggregating, the decreasing time scale and increasing length scale for diffusion will rapidly terminate equilibration of the silicates with the metal (Stevenson, 1981). A possible limit on the effective degree of partial melting is \( F = 0.22 \), where crystalline grains will no longer remain in contact with each other at the intergranular faces (Stocker and Gordon, 1975). The investigation by Walker, Stolper and Hays (1978) of the stability of the terrestrial low-velocity zone may also be relevant to this question. They found that for \( F = 0.1 \) the terrestrial low velocity zone could be largely drained of melt on a time scale of centuries, although this result is somewhat dependent on the scale of the melting system. Because of the large density difference between metal and silicate, a value of \( F < 0.1 \) may be reasonable for the degree of partial melting during metal-silicate equilibration in the Moon, although the Moon may have continued to melt after effective isolation of the metal phase.

The other critical factor is D(W), the solid-metal/silicate-melt partition coefficient for the Moon. D(W) depends strongly on the
oxidation state of the Moon, which is related to the FeO content of the silicates and the Ni content of the metal in the Moon. The two scales plotted on the right ordinate of Fig. 11 show the relationship between D(W) and the FeO content of the silicates for both 6% Ni and 52% Ni in the metal. Six percent Ni corresponds to the assumption that the Ni-Fe ratio in the metal is approximately the cosmic ratio. Fifty-two percent Ni assumes a chondritic relationship between Ni content of the metal phase and total metal content (Anders, 1964). The actual Ni content of metal in the lunar interior probably falls within these limits. Model lunar compositions cover a wide range in FeO content (2.3 to 13.9%), corresponding to a large range in D(W) (Warren and Wasson, 1979). Most of the recent model compositions tend towards higher values of FeO corresponding to lower values of D(W).

Figs. 11 and 12 may be used to examine the conditions under which the depletion of W in the Moon could be explained by partitioning of W into metal within the Moon. The conditions discussed by Rammensee and Wänke (1977) are a relatively high FeO content (13%), which corresponds to a low D(W) of 53, and total melting of the silicates (F = 0.98 in Fig. 12). For these conditions Fig. 11 illustrates that a small metal content consistent with geophysical constraints could not be responsible for the observed depletion of W. We have argued, however, that equilibrium of silicate phases with metal at high degrees of partial melting is geologically unlikely. The situation at low degrees of partial melting is illustrated in a different way in Figs. 12a and
12b. These figures are derived directly from Fig. 11 for 6% Ni and for 52% Ni in the metal respectively. Fig. 12a shows for the assumption of 6% Ni in the metal that reasonable lunar depletion factors (Table 6) can be achieved for lunar FeO contents as great as 13%. Fig. 12b shows for the assumption of 52% Ni in the metal that reasonable depletion factors can be achieved only if the lunar FeO content is less than 6% to 8%.

The actual ranges of values of D(W) and F which are consistent with the lunar depletion of W are uncertain due to the wide range in possible lunar depletion values (Table 5) and the uncertainty in the FeO content of mafic silicates and Ni content of metal in the moon. The only situation where the low W/La ratio in the Moon could not be explained by a 2% metal core is the combination of a high lunar FeO content with a very high Ni content in the metal. Even this constraint would be greatly relaxed if a core somewhat larger than 2% metal exists.

Of less importance is the variation in the modal composition of the Moon for different lunar bulk compositions. Compositions with low FeO contents tend to have high normative plagioclase contents. A large amount of plagioclase reduces the metal/total silicate somewhat at low degrees of partial melting, because plagioclase may have a higher solid-silicate/silicate-melt partition coefficient for W than does olivine or pyroxene.

Phosphorus

The Moon has the lowest P/La ratio among the Earth, Moon and EPB. The low P/La ratio represents a reduction by a factor of approximately 115 relative to Cl chondrites (Table 5). I have shown above that the
low W/La ratios in the Moon can be achieved by metal-silicate equilibration and separation of metal at low degrees of partial melting during early lunar differentiation. This conclusion may be tested for consistency with the observed P/La ratios in the Moon.

In order to obtain the large P/La depletion factor for the Moon, partitioning of P into a metallic liquid is necessary, as solid-metal/silicate-melt partition coefficients are too low. At conditions appropriate to lunar petrogenesis (1300°C and log fO2 correlated with FeO-content) the concentrations of P and S in lunar metal are probably sufficient to allow complete melting of the metal. To achieve the large P/La depletion in the Moon a relatively high concentration of P (≈7 wt%) is needed in the metal, if the initial P concentration is approximately chondritic (1300 ppm). At this P concentration and with reasonable Ni contents, the presence of S is not even required to completely melt the 2% metal content at a temperature of 1300°C. For lunar conditions, therefore, the required S content is sufficiently low that a solid-metal/metalllic-liquid partition coefficient of 0.12 can be assumed (Narayan and Goldstein, 1982). Larger S concentrations may increase this value as noted in Chapter 3.

The calculations for the Moon plotted in Figs. 13a and 13b were calculated assuming partitioning of P into a metallic liquid which was low in S at 1300°C. Assuming a total lunar metal content of 2%, these figures illustrate the combination of FeO content and degree of partial melting required to achieve a reasonable P/La depletion factor for the
Figures 13a,b. Combination of percent partial melting and FeO content at 1300°C required to achieve a reasonable P/La depletion factor for the Moon. -- Lunar P/La depletion factors are listed in Table 6. Fig. 13a is for 2% liquid metal containing 6% Ni, Fig. 13b is for 2% liquid metal containing 52% Ni. The figure is constructed by calculating the P and La concentrations in the silicate liquid for different degrees of partial melting (equation 3.7), from which the P/La depletion factor relative to the initial P/La ratio is calculated. The metallic-liquid/silicate-melt partition coefficients were determined by first calculating the log fO₂ for various FeO contents and Ni contents using equation 3.6. From the log fO₂ the partition coefficients D(P) were calculated from the experimental relation for 1300°C (equation 3.6). The metallic-liquid/silicate-melt partition coefficients were then calculated, assuming a solid-metal/metallic-liquid partition coefficient of 0.12 (Narayan and Goldstein, 1982). The model lunar silicate composition used was from Taylor and Bence (1975). The silicate mineral partition coefficients for P are listed in Fig. 4.
Figure 13a  Combination of percent partial melting and FeO content at 1300°C required to achieve a reasonable P/La depletion factor for the Moon.
Figure 13b  Combination of percent partial melting and FeO content at 1300°C required to achieve a reasonable P/La depletion factor for the Moon.
Moon (Table 5). Fig. 13a is constructed assuming 6\% Ni in the metal, resulting in a Ni/Fe ratio close to the cosmic Ni/Fe ratio. The calculations in Fig. 13b assume 52\% Ni in the metal, following the relationship between Ni content and total metal content for the ordinary chondrites (Anders, 1964). The actual Ni content of metal in the Moon probably falls within this range.

Fig. 13a shows that a reasonable P/La depletion factor (≈115) can be obtained for lunar FeO contents between 6\% and 13\% assuming equilibration and separation of metal at a degree of partial melting (\(P\)) between 0.15 and 0.01 respectively. Model lunar compositions have a wide range of FeO contents, but recent models favor higher FeO contents of approximately 13\% (Warren and Wasson, 1979). Therefore, assuming a relatively low Ni content in lunar metal, and assuming most of the metal equilibrates and separates from the silicates as a metallic liquid, the low P/La ratios in the Moon can be explained by a geophysically reasonable lunar metal content.

In Fig. 13b the case for a high Ni content and for oxygen fugacities higher than in Fig. 13a is examined. For these conditions only the more reduced (lower FeO) lunar compositions are consistent with a geophysically plausible metal core. A third possibility, not illustrated, is the depletion of the P/La ratio by the separation of solid metal. The separation of solid metal containing 6\% Ni at 1190°C results in a figure very similar to Fig. 13b. Again, only the more reduced lunar compositions are consistent with a small lunar metal content.
These calculations for P are in accord with the calculations for W. The calculations for W are valid for the partitioning of W into either solid or liquid metal, because the preliminary experiments of Jones and Drake (1982) indicate that the solid-metal/metallic-liquid partition coefficient for W is near unity if the S-content is less than approximately 10 wt%. A comparison of Fig. 13a, based on the partitioning behavior of P, with Fig. 12a, based on the partitioning behavior of W, demonstrates a good agreement between the combinations of FeO content and degree of partial melting required to achieve the observed depletions of P and W. For example, assuming 13% FeO in the Moon and 6% Ni in the metal, the depletion factors for the W/La ratio and the P/La ratio (Table 5) can be achieved by metal-silicate separation and core formation during early lunar differentiation at a degree of partial melting between two and four percent.

A major question regarding depletion of P and W during partial melting is explaining the very homogeneous W/La and P/La ratios in lunar samples. Figs. 12 and 13 illustrate the large sensitivity of the depletion factors, and therefore the W/La and P/La ratios, to small changes in the degree of partial melting. Several factors may help explain this problem. A closer look at the actual mechanism of metal segregation is needed. Assuming that the metal grains are not all the same size, the partitioning of W and the settling of metal grains probably occurs over a significant range in the degree of partial melting. This suggests that an important control on the depletion of W
is the size-frequency distribution of metal. A relatively constant size-frequency distribution and metal content of accreting material may lead to a relatively constant W/La ratio. Other mechanisms following core formation could also lead to homogenization. These include convection and the possible formation of a lunar magma ocean.

5.2 Origin of the Moon

A possible similarity between the abundances of siderophile elements in the Moon and Earth has led to suggestions that the Moon formed from the Earth's mantle following terrestrial core formation (Delano and Ringwood, 1978; Ringwood, 1979). This theory has been supported by arguments, which have been shown above to be invalid, that a lunar metal core would be too small to account for the low P/La and W/La ratios in the mantle and crust of the Moon (Rammensee and Wänke, 1977; Ringwood, 1979). The P/La and W/La ratios for the Moon and Earth provide an excellent basis for examining this hypothesis.

A comparison between the W/La ratios in the Earth and Moon indicates these ratios are essentially indistinguishable (Rammensee and Wänke, 1977; Jagoutz et al., 1979). However, the amount of W/La data for terrestrial samples is extremely small.

The P/La ratio in the Earth is significantly greater than the P/La ratio in the Moon (Fig. 4, Table 5). Ringwood (1979) notes that the P/La ratios for the Earth and Moon differ by a factor of two, which he considers to represent a close similarity between the two objects. The P/La ratios are much better known than the absolute abundances of
other siderophile trace elements and the difference of a factor of two in P/La ratios between the Earth and Moon cannot be lightly dismissed.

Fission of the Moon from the Earth requires explanation of the compositional differences between the two bodies, in particular, the large difference in FeO contents, in addition to differences between P/La ratios. Ringwood (1979) explained the difference in FeO contents by incorporating in the Moon part of a terrestrial magma ocean that has been enriched in FeO by crystallization. This mechanism does not explain the difference in P/La ratios, because the P/La ratio in a terrestrial magma ocean would be the same as in the bulk Earth. To explain the difference in FeO contents, Jagoutz and Wänke (1982) have proposed a mechanism involving disproportionation of FeO over geologic time, to reduce the FeO content in the Earth to its present value from an originally lunar value. This would require, however, the concomitant transfer of P from the core out to the mantle, and efficient mixing of the mantle, to explain the present difference in P/La ratios.

An independent origin of the Moon, separate from the Earth is consistent with the results of this study. The depletion of siderophile elements in the Moon, including both P and W relative to La can be attributed to partitioning of the elements into a small, geophysically plausible lunar core. The large compositional differences between the Earth and Moon, such as the FeO contents and the P/La ratios, are difficult to reconcile with a terrestrial origin of the Moon.
CHAPTER 6

METAL-SILICATE FRACTIONATION IN THE EARTH

In the previous section we showed that the P/La and W/La ratios in the Moon were probably established by internal processes, rather than by external processes that occurred prior to formation of the Moon. For the Earth, the general assumption is that the P/La and W/La ratios were established only by internal processes. The P/La ratios in the Earth are depleted relative to Cl chondrites by a factor of approximately 40 (Fig. 4), while W/La ratios are depleted by a factor of approximately 19. The Earth's core comprises 30 wt% of the Earth and at present consists of a liquid outer core and a solid inner core that represents less than 7% of the total core. The liquid outer core contains a small amount of a light element, the nature of which is at present controversial (Stevenson, 1981; Ringwood, 1979).

An important consideration for the Earth is the pressure at which the siderophile abundances in the present upper mantle were established. Ringwood (1979) has long advocated establishment of metal-silicate equilibrium at the core mantle boundary, but this requires whole-mantle convection to effect the siderophile abundances in the upper mantle. Recently Stevenson (1981) has advocated establishment of metal-silicate equilibrium at relatively low pressures during core formation. He suggests that core formation began when the growing proto-Earth was approximately the size of Mars and that the rapid settling of
large iron blobs through the mantle prevented significant diffusion at great depths between the iron metal and the mantle.

The larger metal content (30%) and lower FeO content (7% to 11%) in the Earth compared to the Moon suggests that a lower metal/silicate partition coefficient is needed to explain the smaller P/La depletion in the Earth. The calculations plotted in Fig. 14 assume low pressure equilibration and separation of solid metal at 1190°C, for various FeO contents. The calculations in Fig. 14 suggest that low pressure partitioning of P can explain the reduced P/La ratios in the Earth only if the equilibration occurred at very low temperatures and relatively large degrees of partial melting, an apparent paradox.

The relatively small depletion of W/La ratios in the Earth is even more of a problem because $D(W)$ is greater than $D(P)$ under the conditions used for the calculation in Fig. 14, but the W/La depletion is less than the P/La depletion. It is not possible, therefore, to construct an internally consistent model to explain the P/La and W/La ratios in the Earth, in contrast to the Moon and EPB.

Several explanations are possible for the failure of the equilibrium partitioning models to explain the P/La and W/La ratios in the Earth. Many other siderophile elements, while depleted relative to chondrites, are known to be overabundant for equilibrium with a metal phase in the Earth's mantle (Jones and Drake, 1981). One common explanation is a late veneer of material during accretion, where siderophile elements were not removed to the Earth's core (Kimura, Lewis and Anders, 1974). Another possibility is that even with
Figure 14. Combination of FeO content and degree of partial melting required to achieve the P/La depletion factor for the Earth, for partitioning of P into solid metal at 1190°C. -- The calculations were performed as in Fig. 13a,b assuming 6% Ni in the metal and a temperature of 1190°C. The silicate phase assemblage assumed for the calculation is based on the norm of pyrolite III (Green and Ringwood, 1967). The phase assemblage is: plagioclase 8.9%, high-Ca pyroxene 4.9%, low-Ca pyroxene 11.3%, olivine 44.9%, solid metal 30%. 
Stevenson's (1981) core formation model, pressures during metal-silicate equilibrium were sufficient to change the partitioning behavior. The last possibility, favored by Ringwood (1979), is equilibrium at extremely high pressures where disproportionation reactions or the solution of oxygen in the core may drastically change metal-silicate partitioning behavior.
CHAPTER 7

CONCLUSIONS

7.1 Eucrite Parent Body

The experimental determination of the partitioning of W and P between solid metal and silicate melt as a function of temperature and oxygen fugacity provides an additional tool for investigating the composition and early history of the Earth, Moon and Eucrite Parent Body. To explain the depletion of the P/La ratio in the eucrites relative to Cl chondrites by a factor of 40 with a model that is consistent with the results for W requires partitioning of W into 2 to 10% solid metal. The constraints from the P/La ratios require an additional 5% to 25% S-bearing metallic liquid. The required contents of both solid metal and metallic liquid are proportional to the degree of partial melting of the silicates during metal-silicate equilibration. These conclusions are consistent with the following geologic history of the EPB:

1. Accretion of a relatively homogeneous asteroidal sized EPB.

2. Equilibration of P and W with 5% to 25% S-bearing metallic liquid, and 2% to 10% solid metal, at a low degree of partial melting of the silicates.

3. Separation and isolation of metal from silicate phases. The separation of metal lowered the W/La and P/La ratios in the source region silicates.
4. Continued partial melting to generate the primary eucritic magmas.

7.2 Moon

The depletion of P/La and W/La ratios in the Moon relative to Cl chondrites can be explained by partitioning of P into a geophysically plausible (2 wt%) metal core by separation of metal and silicate at low degrees of partial melting. These results, coupled with the evidence that the P/La ratio and the FeO content of the Moon are different from the Earth, are difficult to reconcile with formation of the Moon from the Earth's mantle by fission following terrestrial core formation. An independent origin of the Moon separate from the Earth remains a viable hypothesis (see also Taylor, 1982).

7.3 Earth

In contrast to the case for the Moon and EPB, an internally consistent model involving equilibrium between metal and silicate at low pressures with subsequent separation of metal, cannot be constructed to explain the low W/La and P/La ratios in the Earth. The large mass of the Earth compared to the Moon and EPB raises the possibility of large departures from chemical equilibrium between metal and silicate, and possible pressure effects on trace element partition coefficients.
REFERENCES


eisenreichen ecken der dreistoffsysteme eisen-schwefel-kohlenstoff, 
eisen-schwefel-phosphor und eisen-schwefel-silicium. Giesserei 
Forschung 32, 1-5.


Sonett C.P. and Reynolds R.T. (1979) Primordial heating of asteroid 
parent bodies. In Asteroids (T. Gehrels, ed.), p. 822-848 
University of Arizona Press, Tucson.


Stevenson D.J. and Yoder C.F. (1981) A fluid outer core for the moon and 
its implications for lunar dissipation, free librations and 
magnetism (abstract). In Lunar Science XII, p. 1043-1045. Lunar and 
Planetary Institute, Houston.

Stocker R.L. and Gordon R.B. (1975) Velocity and internal friction in 

Stolper E. (1975) Petrogenesis of eucrite, howardite and diogenite 


Planetary Institute, Houston.


(abstract). In Lunar Science VII p. 898-900. The Lunar and 
Planetary Institute, Houston.

volatile elements and their abundances in ordinary chondrites. 

melt/solid segregation: size of the Eucrite Parent Body and 
Res. 83, 6005-6013.


